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Ian Mallov

AUTEUR DE LA THÈSE / AUTHOR OF THESIS

M.Sc. (Chemistry)

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Department of Chemistry

FACULTÉ, ÉCOLE, DÉPARTEMENT / FACULTY, SCHOOL, DEPARTMENT

Coordination Chemistry of Diindole Ligands:
Synthesis and Reactivity of a Di(indolyl)bicyclononylborate Ligand and Explorations in Main Group Diindolylmethane Chemistry

TITRE DE LA THÈSE / TITLE OF THESIS

Darrin Richeson

DIRECTEUR (DIRECTRICE) DE LA THÈSE / THESIS SUPERVISOR

CO-DIRECTEUR (CO-DIRECTRICE) DE LA THÈSE / THESIS CO-SUPERVISOR

Tom Baker

Deryb Foog

Gary W. Slater

Le Doyen de la Faculté des études supérieures et postdoctorales / Dean of the Faculty of Graduate and Postdoctoral Studies

Coordination Chemistry of Diindole Ligands: Synthesis and Reactivity of a Di(indolyl)bicyclononylborate Ligand and Explorations in Main Group Diindolylmethane Chemistry

Ian Mallov

Thesis submitted to the Faculty of Graduate and Postdoctoral Studies in partial fulfillment of the requirements for the degree of

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In
Chemistry

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University of Ottawa

Candidate	**Supervisor**
Ian Mallov	Professor Darrin Richeson

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Abstract

Chapter One gives a brief overview of established coordination chemistry of pyrrole and indole-based ligands, and of the ansa-metallocene chemistry of ligands featuring a heteroatom in the bridging position. Proposals for syntheses of coordination compounds of two different ansa-indolyl ligand systems are outlined.

Chapter Two describes the synthesis and characterization of an anionic diindolylborate ligand and outlines attempted reactivity with transition metal and main group halides. Spectroscopic results from these reactions as well as reactions to synthesize variants of this ligand are presented. The final section details syntheses of variants of a known diindolylmethane ligand.

Chapter Three presents the first well-characterized Group 13 coordination compounds of the di(3-methylindol-2-yl)-4-bromophenylmethane ligand. Hydrogen-elimination reactions producing borane and alane complexes in high yield were employed. Spectroscopic characterization is presented, as well as solid-state structural characterization of the borane. Further reactivity with trimethylaluminum is explored but results are not as definitive.

Chapter Four details the first explored reactivity of the diindolylmethane ligand with metals from the s-block. Dinuclear compounds of lithium, sodium, and potassium were obtained by reaction of di(3-methylindolyl)-4-bromophenylmethane with common amides of the metals. All three compounds proved reactive with metal halides and their utility as precursors to further coordination complexes was demonstrated by reaction with calcium iodide. The potassium salt yielded a calcium complex of di(3-methylindolyl)-4-bromophenylmethane, the first known Group 2 complex of diindolylmethane. .

Chapter Five explores reactivity with Group 15 phosphine and stibine reagents. Phosphine halides of both di(3-methylindolyl)-4-bromophenylmethane and di(3-methylindolyl)-4-fluorophenylmethane were synthesized and characterized spectroscopically. A solid-state structure of di-(3-methylindol-2-yl)chlorophosphine-4-bromophenylmethane was obtained. The purposes of targeting these compounds was to establish diindolylmethane as a viable supporting framework for Group 15 compounds, to examine relative Lewis basic properties of the diindolylmethane ligand system, and to determine if they were a suitable route to phosphenium cations. A diindolylmethane complex of an amidostibine was also obtained and characterized by spectroscopic and elemental analysis. Attempts toward both phosphenium and stibenium cations through halide abstraction and substituent protonation, respectively, did not yield the expected cations.

Acknowledgements

It is standard practice to say, with regards to any involved work, that completion would not have been possible without the support of a large number of people. In my case, with regards to this thesis and candidacy for a M.Sc. in inorganic chemistry, I think this is especially true.

First and most closely associated with this work, are my supervisor and labmates with whom I have had the pleasure to work for the past two years. Dr. Darrin Richeson's patience, flexibility, and optimism have allowed what began as a somewhat frustrating endeavour to end with a sense of fulfillment. I would also like to thank him for giving me, a B student in undergrad, an opportunity to prove and improve myself through continued education in chemistry. As I've found with all learning, you never realize you're doing it until you look back later and realize you think differently. Thanks to Darrin for giving me the opportunity to think differently today than I did two years ago. Also thanks to my labmates: Nat Lavoie, whom I contacted for information before I came to the lab and from whose advice I continued to benefit right up until today; Dom Duguay (we'll leave nicknames out of this), who arrived from the Maritimes at the same time as I did and submits her own thesis at the same time; Jessica Priem, whose Chretien-esque dismemberment of both official languages has provided ample material for the Richeson Group Facebook quote board; Titel Jurca, who disproved the theory that the amount of hockey pool trash talk should be proportional to the amount of winning; Ahmed Saad, for among other things, an awesome new addition to my wardrobe; and undergrads Jon Gilchrist , Justin Lummiss, Ben Chung, and Katrin Blank. In addition, thanks are due to

the rest of the Marion crew, and the members of the CGSA with whom I had the pleasure of working.

I would also like to thank the faculty and staff for support, in particular: Dr. Tara Kell and Dr. Muralee Murugesu for patiently donating their time and expertise to help teach me some preliminary crystallography; Dr. Ilia Korobkov and Dr. Glenn Yap (as well as Dr. Tara Kell) for solving the x-ray structures and coaxing those R-values down; Dr. Glenn Facey and Cheryl McDowall for NMR expertise; and of course Dr. Deryn Fogg and Dr. Tom Baker who both cheerfully agreed to read this manuscript on short notice despite busy schedules.

A number of people from my days at Dalhousie also merit mention, because without their friendship and support through my undergraduate degree I would never have had this opportunity. My undergraduate supervisor Neil Burford, and the Burford and Stradiotto grad students at Dal, 2002-2006, whom I had as TA's throughout my four years there and who took an exceptional interest in an undergrad and helped me all the way through. Heather Spinney, who was responsible for my decision to come to Ottawa U. My undergrad classmates, especially the crew of: Malcolm, Adam, Alex, Mark and Rebecca.

I would like to thank Jess for enduring my frustrations, as well as for making the good times during my two years here that much more enjoyable.

Lastly, I thank my parents for encouraging education and my whole family for unending moral as well as sometimes financial support.

Chapter 1

Introduction to Indolyl Ligands and Ansa-Metallocenes

I Pyrrole and Indole-Based Ligands

II Bridged Metallocenes

III Diindolylmethane Ligands and Their Coordination Chemistry

INTRODUCTION

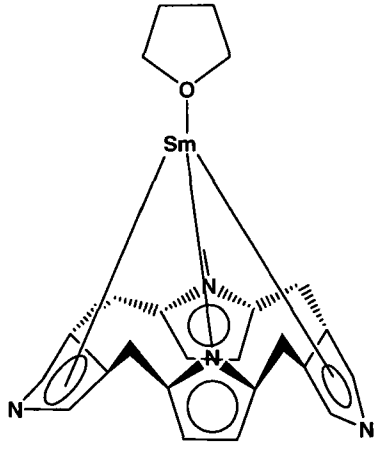
I: Pyrrole and Indole-based Ligands

The variety of N-based ligands to be found in the literature serving a range of purposes can be attributed to the many possible coordination modes of nitrogen depending on the nature of the ligand into which it is incorporated. Coordinating to main group and transition metal elements by forming covalent σ bonds, by dative σ-donation, by σ- and π-donation, and participating in π-donation from delocalized systems such as aromatic heterocycles are all common (**Figure 1.1**).

Figure 1.1: General co-ordination modes of nitrogen

Pyrrole and pyrrole-derived moieties are common nitrogen-donating ligands. Further, several examples featuring multiple pyrrolyl moieties in ligands are known including Dolphin's late transition metal poly-dipyrromethene complexes[1], dipyrromethane and calyx-tetrapyrrole complexes of samarium **1.1** and niobium by Gambarotta[2], di(2-pyrrolylmethyl)amine complexes of titanium by Odom **1.2**[3], dimethylaminomethylpyrrolyl complexes of aluminum by Huang **1.3**[4], an imino-pyrrolide

complex of titanium by Fujita **1.4**[5] and a tris(dimethylpyrrolyl) complex by Schrock **1.5**[6] are some examples.



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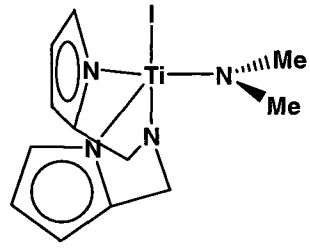

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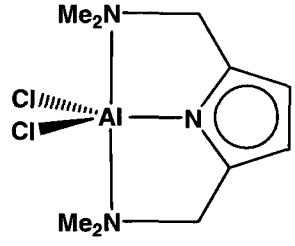

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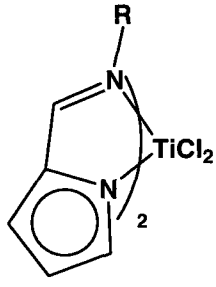

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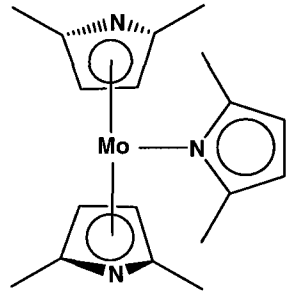


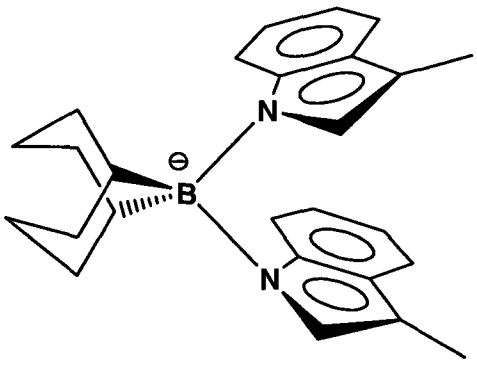
1.5

By varying the substitution of the pyrrolyl moieties and hence the sterics and electronics of the ligand system, it is possible to induce a preference for σ- or π-binding coordination modes as well as tune the Lewis basicity of the nitrogen atom.

Indoles are a pyrrole variant less commonly used as coordinating moieties in ligands than some alkyl-substituted pyrroles. The benzene ring of indoles is planar, electron-withdrawing, precludes reactivity of the pyrrole ring at two positions, and

extends the pyrrole π-system. These fundamental alterations make indole-based ligands distinct from alkyl-substituted pyrrole ligands. Examples of indole moieties coordinating to main group, transition metal, and lanthanide or actinide centres via π-donation, most commonly in η^5 fashion from the pyrrole system, as well as σ- and π-donation are known.[7]

This thesis will examine the synthesis and chemistry of two distinct classes of indole ligands: diindolylbicyclononylborates **1.7**, designed for π-coordination of metals, and diindolylphenylmethanes **1.8**, designed to be deprotonated and coordinate in a σ–fashion through nitrogen.



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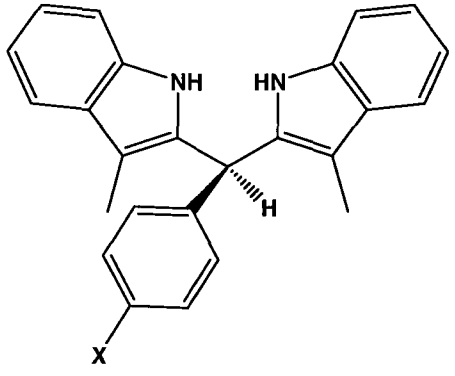


1.8

II: Bridged Metallocenes

Since the discovery of ferrocene in the early 1950's, a wide range of metallocene complexes have been synthesized featuring many different transition metals as well as main group, lanthanide and actinide atoms. The first examples of these complexes featured the cyclopentadienyl (Cp) ligand, but gradually the ligands have evolved as well to include a range of arenes as well as complexes with one arene ligand and one or more

non-arene ligands. While many of these complexes have found uses in themselves in everything from fuels to pharmaceuticals, perhaps the most widespread application of this class of molecule has been in catalyzing chemical transformations. Of these, olefin polymerization is perhaps the most significant and well-known. Electron-deficient complexes with cationic metal centres and alkyl as well as aryl ligands have been shown to be active species in olefin polymerization.

A significant evolution of metallocene chemistry over the last two decades has focused on synthesis and reactivity of so-called ansa-metallocenes, where one or more atoms covalently link two coordinating moieties (often aromatic rings) of metallocene complexes. Bridging the metallocene complexes alters the angle at which the orbitals of the two coordinating parts interact with the metal to which they are coordinating (**Figure 1.2**).

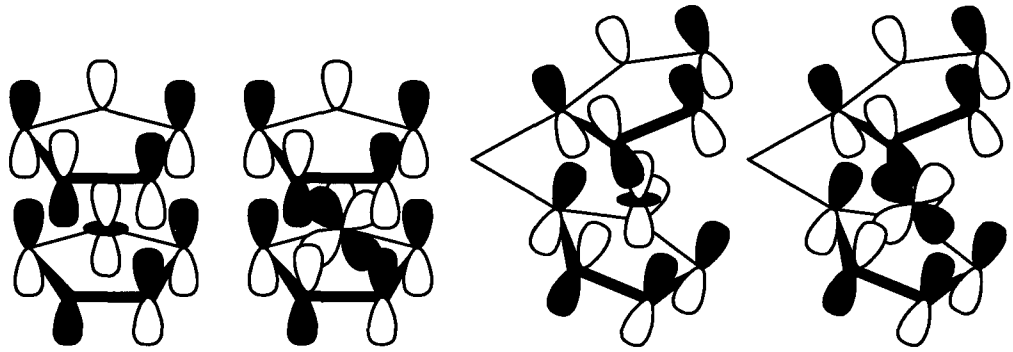
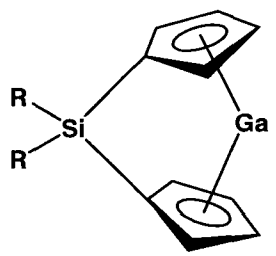


Figure 1.2: Overlap of ligand p-orbitals with metal d-orbitals in bridged (right) and unbridged (left) metallocenes

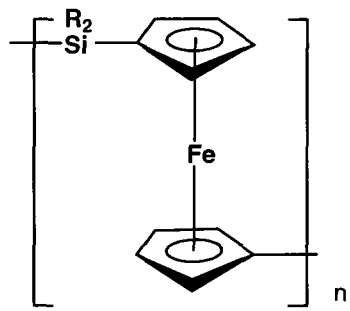
While carbon-based bridges are most popular, ansa-metallocene complexes featuring main group heteroatoms in the bridging position have become increasingly common. The bridging atom itself can modulate the ligand interactions by changing

either the electron-donating or -withdrawing ability of the ligand. This in turn can change the electronics at the metal centre. Examples of main group atoms bridging metallocenes include silane-bridged ferrocenyl monomers **1.9** and polymers **1.10** by Manners[8], monoanionic gallate- **1.11** and aluminate- **1.12** bridged molybdenum complexes by Muller[9], borate-bridged zirconium complexes by Bochmann **1.13**[10], as well as the use of the phenyl rings of the commonly-used counterion tetraphenylborate to coordinate to niobium **1.14** by Pampaloni[11] and lanthanides by Deacon and Junk.[12]



1: R = Me
2: R = Ph

1.9



1: R = Me
2: R = Ph

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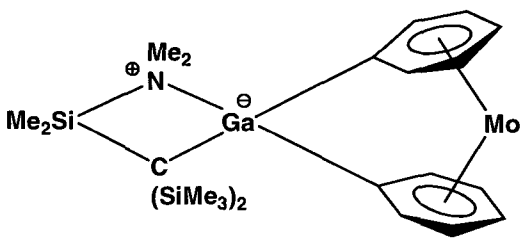

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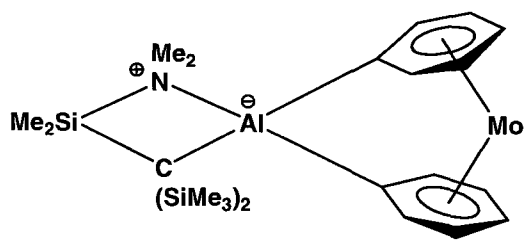

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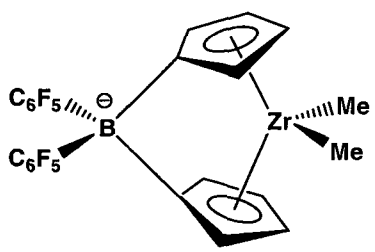

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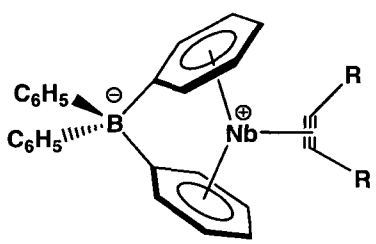
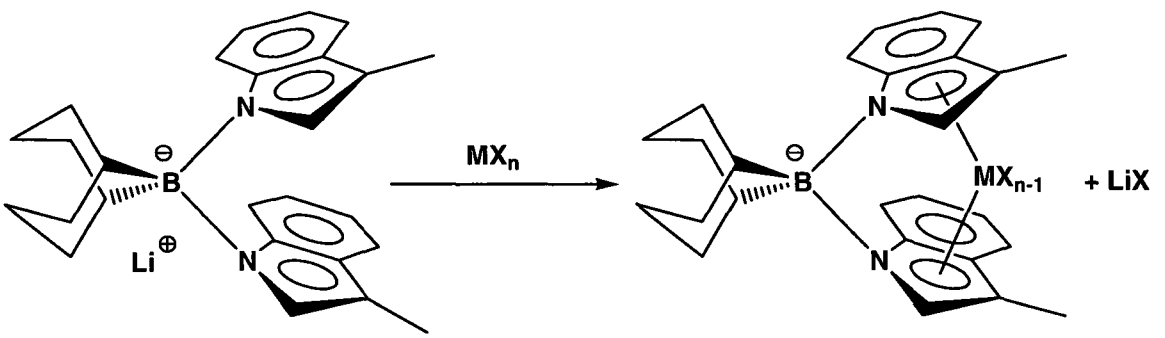


1.14

Bridged indole rings coordinating to metals, however, are to the best of our knowledge unknown in the literature. Due to the aforementioned pyrrole π-complexes of metals, as well as the examples of Group 13-bridged anionic ansa-metallocenes known, we proposed to investigate the utility of borate-bridged indolyl complexes in reaction with early transition metals to determine if new ansa-metallocene complexes would be formed (**Scheme 1.1**), and to investigate any catalytic properties these potential complexes might exhibit. The reactive 3-position of the indole rings is protected with a methyl group to ensure coordination of boron through the nitrogen atom during synthesis of the ligand. The lithium salt **1.15** of this anionic ligand is pictured.



1.15

Scheme 1.1: Potential synthesis of early transition metal complexes of di(3-methylindolyl)bicyclononylborate

Testing the reactivity of this type of ligand with early transition metal compounds in high oxidation states seemed like the most promising avenue of investigation. The rich previous history of early transition metal metallocene complexes and the abundance of readily available d^0 compounds of Group 3, 4, 5 and 6 metals, whose electron deficiency has the dual advantage of making them electrophilic to facilitate π-binding and

diamagnetic to more easily analyze reactions by NMR, were the major factors in directing our efforts towards these targets.

Electron-deficient main group complexes may be accessible as well with this ligand system. Groups 1, 2 and 13 metals in +1, +2, and +3 oxidation states, respectively, would also be electrophilic, diamagnetic molecules, and there is ample precedent over the last few decades for main group metallocene complexes as well.[12, 13]

As previously mentioned, indolyl ligands have the potential to bind in either a σ or π mode. However, with a ligand where the potentially σ-donating nitrogen atoms are capped by a bridge atom such as boron, π-binding remains the only viable option. Dative σ-donation from nitrogen is highly unlikely as the aromaticity of the pyrrole moiety would have to be broken.

III: Diindolylmethane Ligands and Their Coordination Chemistry

Coordination complexes of main group and transition metals formed by σ-bound anionic pyrroles and indoles have the potential to have significantly greater Lewis acidity at the main group or transition metal atom than analogous complexes featuring common amido ligands. The reduced donating ability of the nitrogen atoms can be mainly attributed to the delocalization of the lone pair of electrons on nitrogen into the aromatic system, as exemplified by resonance forms A-C in **Figure 1.3**. This reduced donating ability results in less electron density at the ligated atom and hence enhances Lewis acidity.

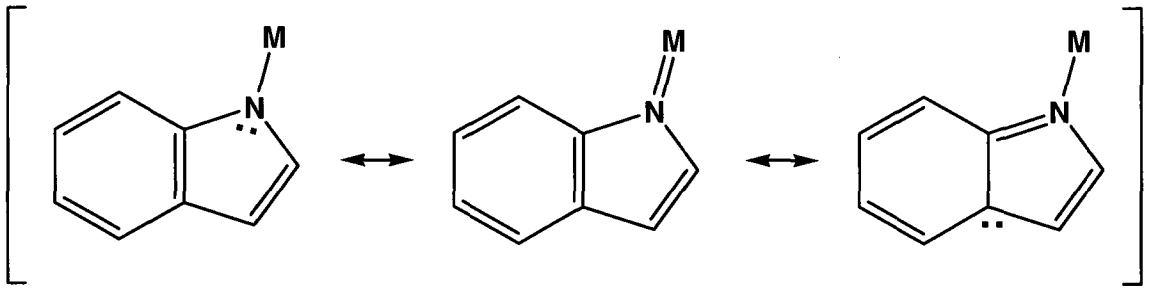


Figure 1.3: Three of the several resonance forms of metal-indolate

Di- and triindolylmethanes are abundant in the literature[13] and are an example of compounds featuring indole moieties which can potentially become σ-donors through deprotonation. The known diindolylmethane ligands are bridged by a carbon atom through the 2-position of the indole and σ-bind to metals through deprotonation of the indole nitrogen atoms. A six-membered heterocyle is thus formed when the nitrogen donors chelate to an atom (**Figure 1.4**).

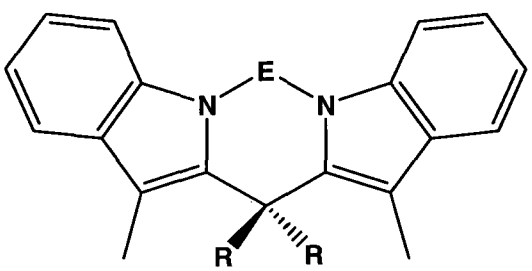
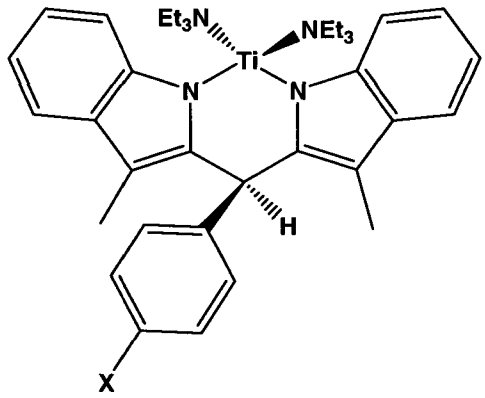


Figure 1.4: Chelating nitrogen atoms of di(3-methylindol-2-yl)methane form a 6-membered heterocycle

Bridging through the 2-position and σ-donation are key features which distinguish diindolylmethane ligands from the di(3-methylindolyl)bicyclononylborate ligand described in the previous section. Structurally, these features make the diindolylmethane ligand likely to be a more rigid system, which affects the geometry of the coordination

sphere of any atom to which they are bound. This has been demonstrated by other similar pyrrolyl ligands such as dipyrromethene ligands.[14]

However, despite the many coordination compounds of the related dipyrromethenes[14], the first reported use of diindolylmethanes as ligands was in 2003 by Mason[15]. Mason synthesized the first transition metal[16,17,18] and main group complexes of polyindolylmethanes[16]. Thus far, however, structurally characterized polyindolylmethane complexes are limited to those reported for titanium **1.16** and zirconium **1.17** amido complexes,[16, 17] and titanium **1.18** and zirconium **1.19** bis(cyclopentadienyl) complexes,[18] triindolylmethane phosphines and phosphine complexes with iron and rhodium **1.20**,[16] and diindolylmethane diphenylsilane **1.21**.[16] Solutions of diindolylmethanes and aluminum alkyls are also reported to homopolymerize epichlorohydrin.[16]



X = H, Br

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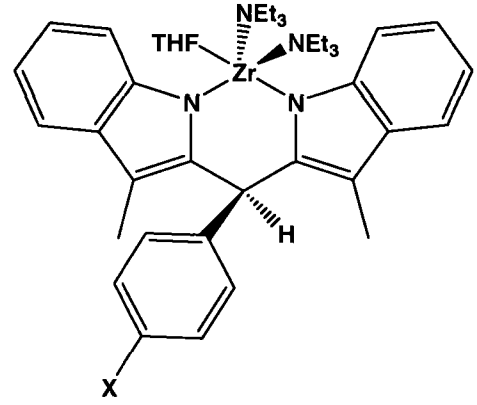
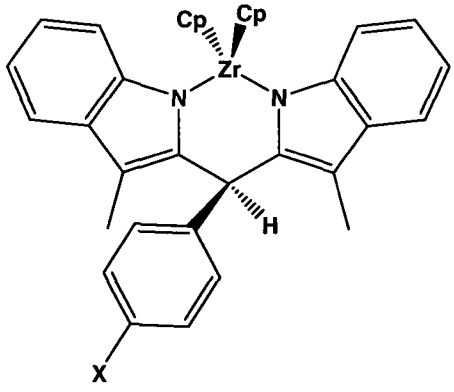


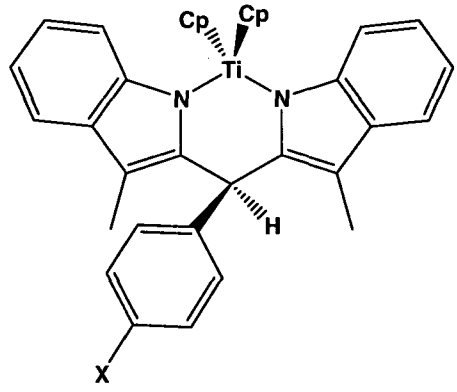
X = H, Br

1.17



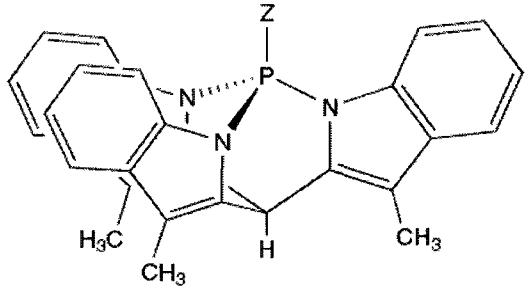
X = H, OCH_3

1.18



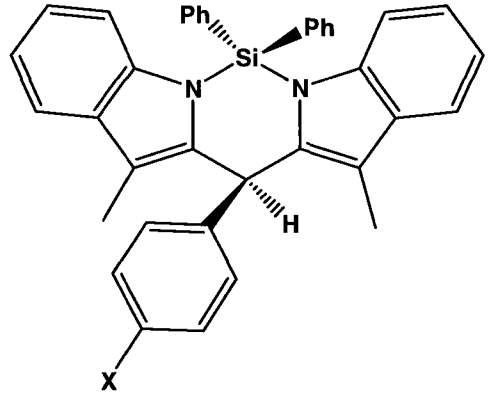
X = H, OCH_3

1.19



Z = Fe, Rh

1.20



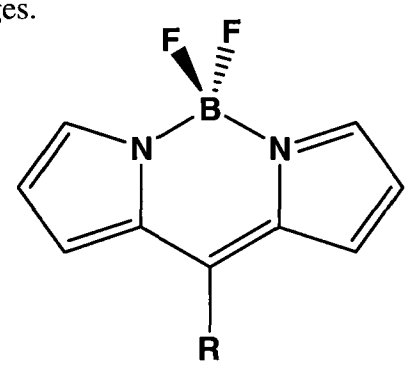
X = H, O-Me

1.21

These investigations, however, are preliminary and cover only a very narrow range of potential molecules: all the complexes are neutral, amido, Cp- or alkyl-substituted and limited to group 4 transition metals and the Group 14 silane. For example, there are no reported Group 1, 2, lanthanide or actinide complexes. This leaves a potentially vast quantity of chemistry to be explored with these types of ligands. This report will include our investigations into the chemistry of diindolylmethane dianions as ligands for Groups 1, 2, 13, 14 and 15 complexes.

Group 1 and 2 complexes of diindolylmethane have the potential to be reactive precursors to other metal complexes as well as fundamentally interesting in themselves. Most commonly, lithium complexes formed from common lithium reagents and magnesium Grignard-type complexes are simple, attractive targets for many types of ligand and we proposed to add diindolylmethane to the library of these types of molecules.

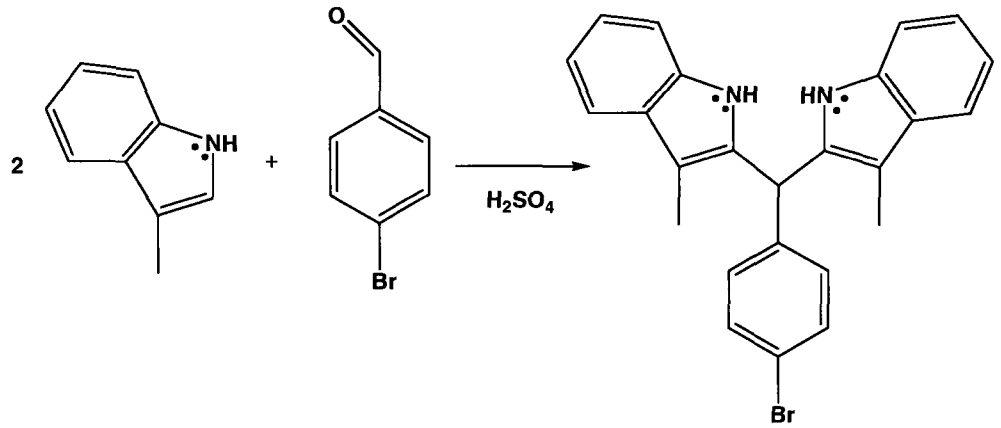
Given the preliminary investigations of aluminum alkyl complexes by Mason, other Group 13 targets are also attractive. The diindolylmethane scaffold bears obvious structural resemblance to the dipyrromethene ligand used to synthesize the family of BODIPY (boron dipyrromethene) dyes **1.22**.[14] Making Group 13 complexes of diindolylmethane similar to BODIPY dyes seemed like a logical extension to this chemistry, with diindolylmethane bearing a formal -2 charge instead of the -1 formal charge of dipyrromethane and therefore potentially forming mono-substituted neutral complexes. These in turn could be precursors, via removal of a halide or hydride, to fundamentally interesting borinium (2-coordinate), borenium (3-coordinate) or boronium (4-coordinate) cations. Analogous investigations of other Group 13 centres also posed interesting synthetic challenges.



1.22

Similarly, Group 15 halides were also attractive targets. Synthesizing phosphorus halides and abstracting the halide to yield a phosphenium cation offered a fundamentally interesting target and would potentially open up the possibility of ligating a phosphorus cation to a metal to further probe the interrelationship of metal and ligand Lewis acid/base properties. Investigating the arsenic, antimony and bismuth chemistry of diindolylmethanes would potentially further expand both the breadth of reactivity of the ligand as well as knowledge of its Lewis acidity and basicity.

Choosing which diindolylmethane ligand to use was the first challenge, as syntheses of many different types, varying primarily at the para-position of the phenyl group, were available in the literature. The facile synthesis shown in **Scheme 1.2** offered a ready means to generate diindolylmethane ligands and was used to synthesize the variants reported herein. The 3-methyl-substituted derivative of indole was used, as the methyl at the 3-position blocks reactivity of the indole π-system and leads to introduction of the phenylmethylene center in the final product through the 2-position of the indole ring. The second major area of investigation of this thesis involves use of diindolylmethane ligands, primarily 4-bromo- **1.23** and 4-fluoro-substituted phenyldiindolylmethanes to substantially expand the chemistry of this ligand system to areas of the periodic table hitherto unexplored.



1.23

Scheme 1.2: A facile synthesis of di(3-methylindol-2-yl)-4-bromophenylmethane **1.23**

The objectives of this thesis are to investigate the σ- and π-coordination chemistry of the diindolylmethane **1.23** and diindolylbicyclononylborate **1.15** ligands, respectively. This involves the synthesis of the lithium salt of diindolylbycyclononylborate, and exploration of its reactivity, as well as extending the reactivity of known diindolylmethane ligands with other main group elements.

Chapter one has outlined the two ligand systems to be investigated, one new, the other with a few known coordination compounds, and outlined the rationale for choosing those two ligand systems.

Chapter two outlines the synthesis and characterization of lithium di(3-methylindolyl) bicyclononylborate. Reactivity with early transition and main group metals is explored, as well as variation of the ligand framework by changing the substitution of the indole moiety or replacing it with substituted pyrroles. Syntheses of two new variants of the diindolylmethane ligand are also presented.

Chapters three through five investigate the coordination chemistry of dianionic diindolylmethane ligands with main group elements of Groups 13 and 14, Groups 1 and 2, and Group 15. Some preliminary explorations of reactivity of these new diindolylmethane complexes are also presented.

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Chapter 2

Ligand Syntheses & Reactions with Diindolylbicyclononylborate Ligands

I Introduction

II Synthesis of Lithium Di(3-methylindolyl)bicyclononylborate

III Reactions of Li [di(3-methylindolyl)bicyclononylborate] with metal halides MX_n

IV Varying the Indolyl Moiety

V Syntheses of New Diindolylmethane Ligands

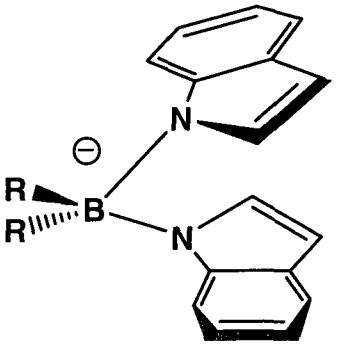
Chapter 2 – Ligand Syntheses and Reactions with Diindolylbicyclononylborate Ligands

I Introduction

Variations of ansa-metallocene ligands featuring heteroatoms in the bridging position, classified into several categories such as metallarenophanes[1] and metallacyclophanes[2] have been employed to π-co-ordinate to metals. The only borate variants presented in the literature have been tetraphenylborate[3,4] and biscyclopentadienyl (Cp) complexes. [5] There is therefore ample potential chemistry to be explored with borate-bridged ligands featuring other arene moieties. Indole groups provide a logical choice to achieve the goal of diversifying the limited library of borate-bridged metallarenophane structures as well as π-coordinating indole-metal complexes.

II Synthesis of Lithium Di(3-methylindolyl)bicyclononylborate

An easy way to bridge two indole rings is to form a covalent bond to the nitrogen atom in the pyrrole ring by deprotonation of the NH moiety and allowing the resulting lone pair to bond to the bridging atom. A monoanionic borate can be formed if each of the four B-bonded substituents has a formal negative charge. By choosing two of these groups to be relatively inert, poor S_N2 leaving groups such as alkyl groups, and two groups to be derived from indole, one would arrive at a structure represented by **X.**



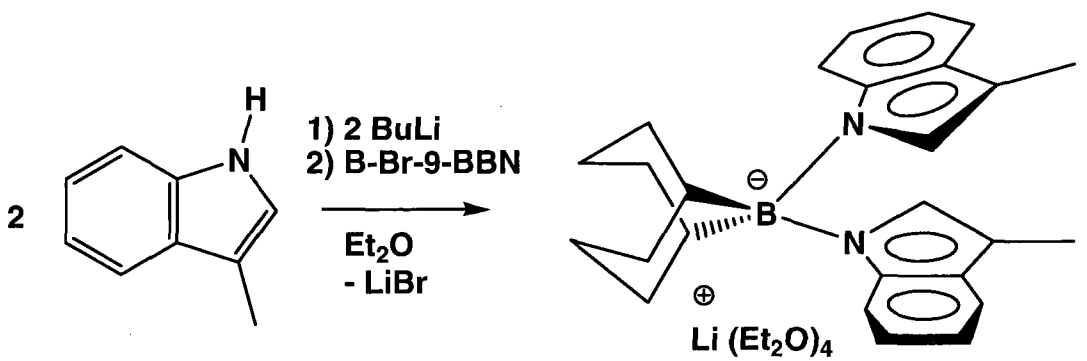
X

Alkyl substituents should not impede either σ-coordination of the indole rings to nitrogen or π-coordination of the indole rings to metals.

9-Borabicyclononane (9-BBN) reagents are common, neutral, inexpensive reagents in which the BBN ring occupies two coordination sites at boron; the third can be occupied by a broad range of substituents. Bromo-9-BBN was therefore chosen as the boron reagent to synthesize the diindolylborate ligand, as it features the BBN substituent as well as bromine, a good leaving group. The 3-methyl-substituted derivative of indole was chosen as the methyl acts as a protecting group at the reactive 3-position.

Deprotonation of two equivalents of 3-methylindole in Et_2O followed by addition of one equivalent of Br-9-BBN in CH_2Cl_2 solution (**Scheme 2.1**) yielded the monoanionic ligand **1.15** after work-up. ^1H,^{13}C and HMQC NMR studies were undertaken to characterize the ligand. The ^1H NMR spectrum showed five clearly defined resonances in the aromatic region and a methyl peak at lower field corresponding to the 3-methylindole moieties and broad alkyl resonances corresponding to the BBN moiety. These integrated to the expected ratio of two 3-methylindole: one BBN moiety. Four equivalents of diethyl ether, which were assumed to be bound to the expected cationic lithium atom, were also visible in the ^1H NMR spectrum. ^1H NMR studies of the salt crystallized from THF indicate four equivalents of bound THF when that is used as the solvent. The ^{13}C NMR spectrum showed eight resonances in the aromatic region corresponding to the indole carbon atoms, four distinct aliphatic resonances corresponding to the three different carbon environments in the BBN backbone and one for the indolyl methyl carbon atom, and two resonances corresponding to the two carbon environments of the coordinated diethyl ether. The coupling in the HMQC spectrum

confirmed these assignments. The solid-state structure was confirmed by x-ray crystallography (**Tables 2.1, 2.2**; **Figure 2.1**). The solid-state structure shows a nearly tetrahedral boron centre, with the C-B-C bond angle of 101.5(3)° and the N-B-N bond angle of 106.9(3)° slightly smaller than in an ideal tetrahedral geometry and the C-B-N bond angles of 110.57(15)° and 113.73(15)° slightly larger. The B-N bond lengths of 1.568(4)Å are in the range expected for B-N bonds of the similar polypyrazolylborate class of ligands.[6] Four diethyl ether molecules are bound to the lithium counterion, in agreement with the ^{1}H NMR spectrum. The solid-state structure shows the indole rings oriented opposite to each other as shown in the product of **Scheme 2.1**, indicating that rotation about the B-N bonds occurs. NMR shows only one set of signals for the two indole rings, indicating that in the solution state at least they are chemically equivalent. However, rotation about the B-N bonds such that the indole moieties adopt the configuration shown in the solid state structure opens up the possibility that there are different structural isomers of **1.15**, as well as potentially different structural isomers of metal complexes formed by a metal binding differently to each indole.



Scheme 2.1: Synthesis of Li [di(3-methylindolyl)bicyclononylborate] **1.15**

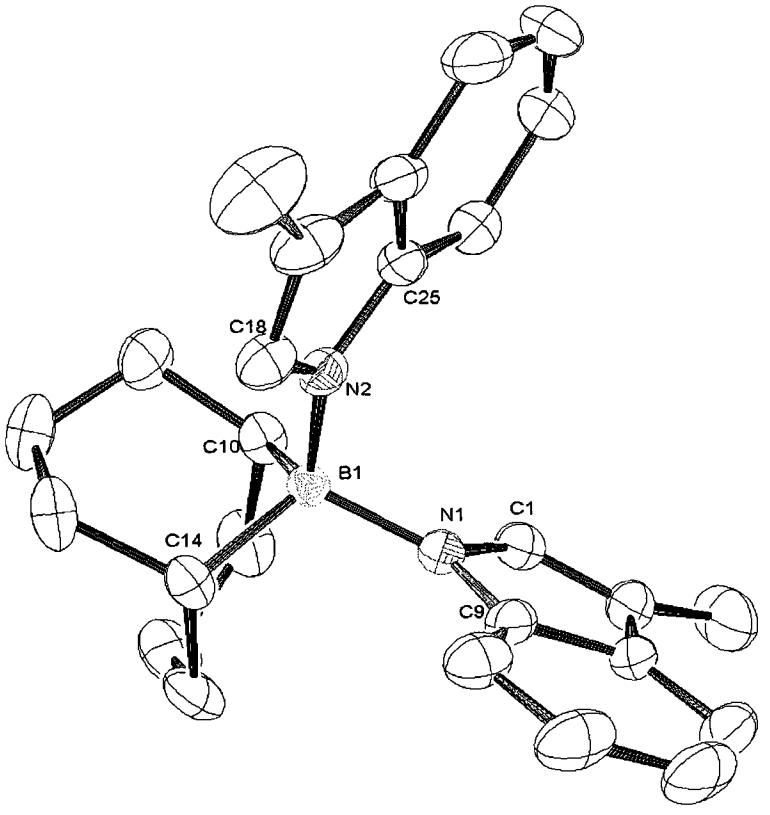


Figure 2.1: Molecular structure and atomic labelling scheme for 1.15

Table 2.1 Selected Bond Lengths (Å) and Angles (deg) for 1.15

A	B	Distance	A	B	C	Angle
B	N1	1.568(4)	B	N1	N2	106.9(3)
B	N2	1.568(4)	C10	B	C14	101.5(3)
B	C10	1.636(4)	C10	B	N1	110.57(15)
B	C10	1.636(4)	C10	B	N2	113.73(15)
Li	O1	1.888(7)	C14	B	N1	113.73(15)
Li	O2	1.888(7)	C14	B	N2	110.57(15)
Li	O3	1.934(6)				
Li	O4	1.934(6)				

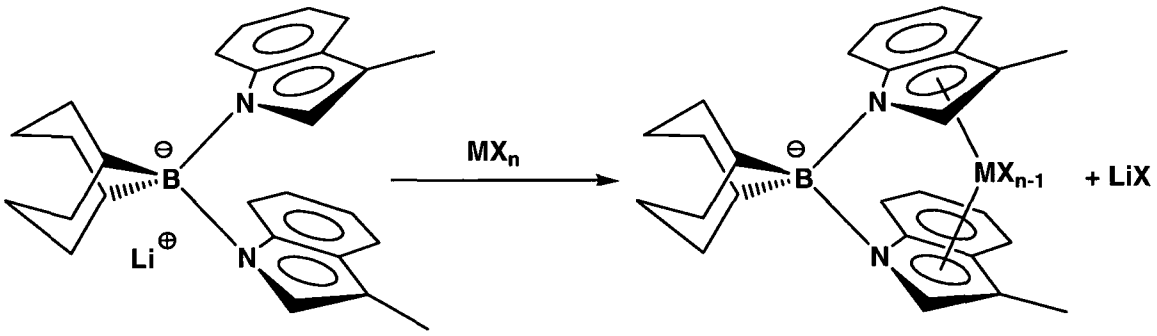
Table 2.2 Selected Crystal Data and Collection Parameters for **1.15**

empirical formula	C_{42} H_{62} B Li N_2 O_4
formula weight	676.69
T (K)	202(2)K
λ(Å)	0.71073
crystal system	tetragonal
space group	$I4_1cd$
a (Å)	15.730(4)
b (Å)	15.730(4)
c (Å)	32.134(17)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	7951(5)
Z	8
Abs. coeff. (mm^{-1})	0.070
Final R indices	R1 = 0.0584
	wR2 = 0.1528

III Reactions of Li [di(3-methylindolyl)bicyclononylborate] with metal halides MX_n

With the lithium salt fully characterized, the next step was to investigate the incorporation of this ligand into the coordination environment of metal centres. Group IV d^0 metals are very commonly used in ansa-metallocene chemistry and these species have proven ability to form complexes which stereoselectively catalyze olefin polymerization and other organic reactions.[7,8,9] There are considerably fewer Group 5 ansa-metallocene complexes known, as most examples synthesized have not demonstrated the catalytic activity that the Group 4 metal complexes have,[10] and therefore development of ansa-metallocene complexes has focused on Group 4 complexes rather than spreading across the periodic table. The limited number of known examples of borate-bridged metallocenophane complexes have all featured Group 4 d^0 metals, as have most of the related metallocene complexes featuring pendant boryl

groups.[11] Early, d^0 transition metals have the advantage of being electron-deficient and therefore having potentially more affinity for π–electron density, as well as facilitating the characterization process by forming diamagnetic complexes with diagnostic NMR spectra. Those two characteristics are shared by Group 13 metals featuring full d-shells as well. For these reasons, the principal avenues of reactivity chosen to be investigated with this ligand were Groups 3, 4, 5, 6 and 13 metal halides, which were proposed to react according to **Scheme 2.2**. Salt metathesis driven by precipitation of LiX has been a successful formula in the preparation of related complexes.



Scheme 2.2: Proposed reactivity of Li[di(3-methylindolyl)bicyclononylborate] **1.15** with metal halides MX_n

The observed reactivity with $ZrCl_4$ and $ZrCl_4(THF)_2$ was in accordance with expectations, as a white precipitate assumed to be LiCl was filtered from reaction of **1.15** with the metal complexes. A yellow solid was obtained from the filtrate, with a ^1H NMR spectrum showing six resonances in the aromatic region slightly shifted compared to those for the free ligand, a broad resonance integrating for ten protons assigned to BBN, two other aliphatic resonances assigned to the ligand, and two more broad resonances assigned to THF. However, repeated attempts to crystallize the yellow solid by a variety

of different methods proved futile and thus single-crystal x-ray diffraction analysis could not be carried out, nor was it possible to obtain the major product in suitable purity for elemental analysis. Reaction of the analogous titanium reagents, $TiCl_4$ and $TiCl_4(THF)_2$ resulted in immediate darkening of the reaction mixture to purple/black. Products indicated in ^1H NMR spectra of the reaction mixtures proved intractable.

Reactivity with Group 3 and Group 13 metal halides was also investigated. In order to probe the potential stability and likely complexes formed from these metals, DFT calculations were carried out on model complexes. Specifically, tris(pyrrole) complexes of Al(III) and Sc(III) were optimized with DFT calculations using the B3LYP functional with the 6-311G basis set. To simplify the computations, pyrrole rings were used in place of the di-3-methylindolyl ligand, and Sc(III) and Al(III), the metals with the fewest electrons in Groups 3 and 13 respectively, were chosen. The obvious limitations to this study were the steric factors imparted by the ligand, primarily the benzene moiety of the indoles, the methyl groups at the 3-position, and the strain caused by the boron bridge. The purpose was primarily to investigate the electronics of the system.

The starting points for the two optimizations were the same with two of the pyrroles oriented in a π fashion and one bonded to the metal in a σ fashion. The optimized structures demonstrate a key difference between the main group metals and the transition metals. The $Al(pyr)_3$ complex optimized with two pyrroles clearly σ bonded through the anionic nitrogen centers (localized anionic charges) as seen in **Figure 2.2**. The third pyrrole is bonded to a pyrrole carbon center. For the $Sc(Pyr)_3$ species, optimization led to two of the pyrroles being π-bonded (more delocalized anionic charge)

and the third σ-bonded through the anionic N center (more localized anionic charge on N) as shown in **Figure 2.3**.

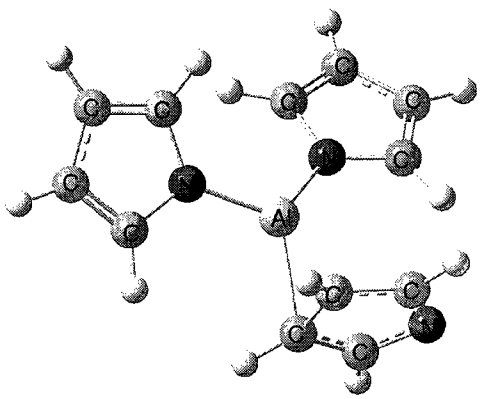


Figure 2.2 Optimized structure for $Al(pyrrole)_3$, $Al(NC_4H_4)_3$

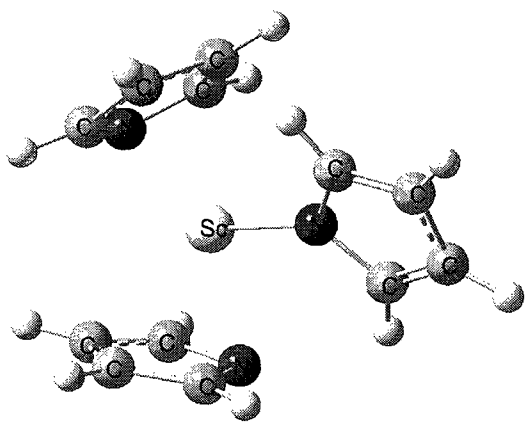


Figure 2.3 Optimized structure for $Sc(pyrrole)_3$, $Sc(NC_4H_4)_3$

Computational investigations also provide a means to examine the viability of group 3 and 13 complexes of the di(3-methylindolyl)bicyclononylborate anion. To this end, a di(3-methylindolyl)bicyclononylborate complex of $Sc(III)Cl_2^+$ was optimized with DFT calculations using the same B3LYP functional and 6-311G basis set. The Sc[di(3-methylindolyl)bicyclononylborate] complex optimized with the Sc centre clearly

π–bonded to the pyrrole rings of the indole, and the two halides residing in the ansa-metallocene wedge (**Figure 2.4**), as is typical for the type of metallacyclophane complex targeted for the ligand. This set of computational results provided encouragement for carrying out reactions of MX_3 (M = group 3 or lanthanides; X = halide) and the lithium salt **1**.

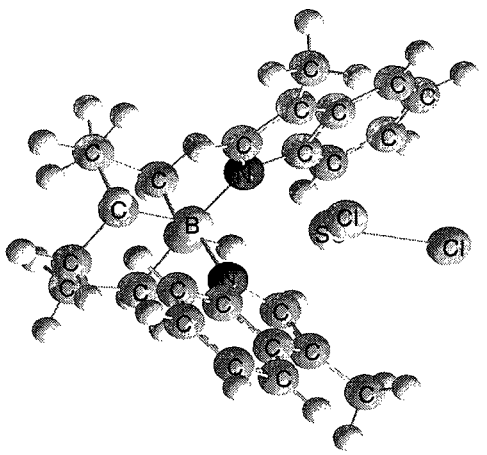


Figure 2.4. Optimized structure for Sc[di(3-methylindolyl)bicyclononylborate] (labels for H atoms are omitted for clarity)

Reaction in THF of Li[di(3-methylindolyl)bicyclononylborate] with YCl_3, a significantly cheaper Group 3 metal than scandium, did not seem to proceed with anion metathesis as suggested by the lack of LiCl precipitation. A major product observed by ^1H and ^{13}C NMR to be different from the free ligand was isolated but crystals suitable for x-ray diffraction analysis have, so far, not been obtained. Reaction of Li [di(3-methylindolyl)bicyclononylborate] with $AlCl_3$ also did not result in precipitation of LiCl but only in a mixture of intractable products. Reaction with $TaCl_5$, $MoCl_6$, WCl_6, similarly resulted only in intractable products.

Pyrrole complexes of lower oxidation-state complexes of chromium by Gambarotta and co-workers[12] indicated that it might be possible to form indole complexes with non-d^0 early transition metals, although there was much less precedent in the literature for these metals in bridged metallocenes and metallacyclophanes. Reaction of Li[di(3-methylindolyl)bicyclononylborate] with $CrCl_2(THF)_{1.3}$ resulted in what appeared to be two products, one purple and the other green. The green product was crystallized and X-ray diffraction analysis indicated that it was a dinuclear chromium complex featuring two bridging chlorides and a bridging oxygen atom bonded to the 9-BBN moiety of the ligand. No 3-methylindole moieties were present, indicating a decomposition of the ligand. The lone bridging oxo ligand indicated either presence of O_2 or H_2O in the system or a ring-opening abstraction of oxygen from THF. The high oxophilicity of boron in either case could have resulted in displacement of the indoles by oxygen at boron.

Additional high oxidation-state main group metal halides were treated with Li[di(3-methylindolyl)bicyclononylborate] including $CaCl_2$, GaI_3, and $InCl_3$. No products from these reactions could be definitively characterized.

IV Varying the Indole Moiety

Success in the synthesis, isolation and characterization of **1.15** prompted further attempts using a range of differently-substituted pyrroles and indoles to synthesize variants of this ligand. Altering the substitution was primarily an effort to vary the sterics of the ligand in an attempt to enhance or at least vary reactivity with metals. It was hoped that variation of reactivity might result in major products which were more readily

isolable and characterizable than the products of the reactions of **1.15** with metal halides. Unfortunately, all of the current attempts resulted in ambiguous complexes. 1,2,3,4-tetramethylpyrrole when lithiated did not undergo the expected reaction with Br-9-BBN. 2-methylindole, 2-phenylindole, and 2,4-dimethylpyrrole were also tested as reagents, and they did prove reactive with the Br-9-BBN reagent. Small quantities of products which were quite impure as determined by ^{1}H NMR were isolated for each of the 2-methylindole **2.1**, 2-phenylindole **2.2** and 2,4-dimethylpyrrole **2.3** variants. The major ^{1}H NMR resonances were close in chemical shift and integration to what was expected for new variants of bicyclononylborate ligands analogous to **1.15**; however, repeated attempts to synthesize these new ligands in sufficient yield and purity to attempt reactions with metal halides were unsuccessful. Attempts were also made to synthesize versions of this ligand featuring tetra-pyrrolyl- and -indolyl substitution **2.4**, with unsatisfactory results.

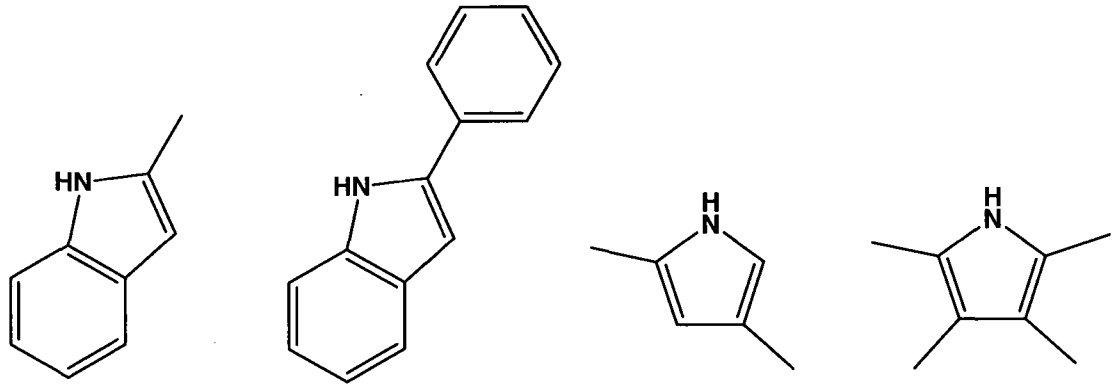


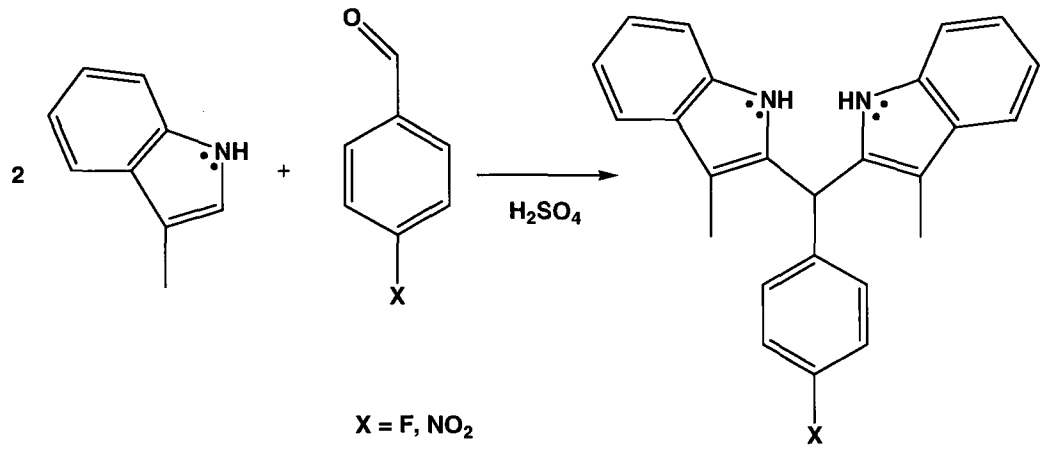
Figure 2.5 The indole and pyrrole reagents with which attempts were made to synthesize new bicyclononylborate ligands

V Syntheses of New Diindolylmethane Ligands

A number of phenyldiindolylmethane ligands with varying substitution at the para position of the phenyl ring have been reported.[13,14,15] Making the substituent more or less electronegative varies the electron-withdrawing ability of the phenyl moiety, and hence the electronics at the phenylmethylene centre (and to a lesser extent the indole rings as well). The simple phenyl(di-3-methylindolylmethane) and the 4-bromophenyl(di-3-methylindolylmethane) species were used by Mason to synthesize titanium and zirconium amido complexes, the most comprehensively characterized of the diindolylmethane coordination compounds. Since an electron-withdrawing group was desirable, the 4-bromo-substituted version was the logical initial choice to continue expanding diindolylmethane coordination chemistry. However, substituting the bromine atom with a more electron-withdrawing group had the potential to affect the chemistry of the ligand. For example, targeting a substituent with greater electronegativity than bromine would potentially increase the acidity of the phenylmethylene proton and enhance the chance of removing it. Targets such as zwitterionic complexes with the nitrogen atoms chelating to a cationic centre and an anionic centre at the indole-bridging carbon achieved through deprotonation would be fundamentally fascinating long-term targets.

By substituting the 4-bromobenzaldehyde reagent with 4-nitrobenzaldehyde and 4-fluorobenzaldehyde, the 4-fluorophenyl(di-3-methylindolylmethane) **2.5** and the 4-nitrophenyl(di-3-methylindolylmethane) **2.6** were attained using the same facile synthetic methods used to produce the 4-bromophenyl(di-3-methylindolylmethane) ligand (**Scheme 2.3**). ^{1}H and ^{13}C NMR was used to characterize these compounds, and some

preliminary reactivity investigations were undertaken which will be discussed later in this thesis.



Scheme 2.3: Synthesis of di(3-methylindol-2-yl)phenylmethane ligands **2.5** (X = F) and **2.6** (X = NO_2)

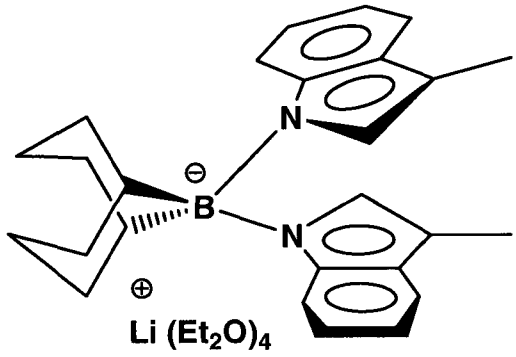
Experimental

General Considerations All manipulations involving polyindolyl or polypyrrolylborate reagents were carried out under nitrogen employing standard drybox techniques. All solvents involved in the manipulations of the polyindolyl or polypyrrolylborate species were sparged with nitrogen and dried by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Deuterated benzene, chloroform and dichloromethane were dried by addition of molecular sieves. Di-(3-methylindol-2-yl)-4-bromophenylmethane was prepared according to a previously reported procedure.[13] $CrCl_2(THF)_{1.3}$ was obtained from Mr. Amir Jabri in the laboratory of Dr. Sandro Gambarotta at the University of Ottawa, who had synthesized it according to a previously reported procedure.[16] All other reagents were purchased from Aldrich and used as received. NMR spectra were run on Bruker Avance 300 and 500 MHz spectrometers with deuterated benzene as the solvent using residual protons of the deuterated solvent for reference.

Syntheses of Lithium Polyindolylborate Ligands

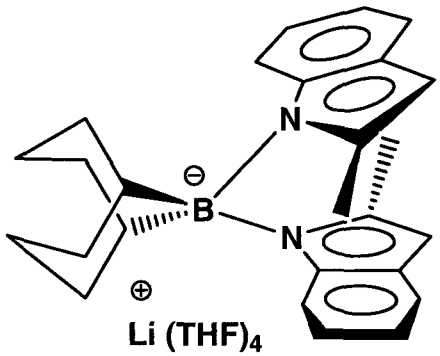
Lithium $(Et_2O)_4$ di(3-methylindolyl)bicyclononylborate **1.15** 3-methylindole (0.338g, 2.58 mmol) was dissolved in 4 mL Et_2O in a vial under nitrogen. Then n-butyllithium (1.60 mL, 2.6 mmol, 1.6M in hexanes) was added dropwise. The solution turned to clear yellow and vigorous bubbling ensued immediately. After stirring for 1 hour 1.29 mL B-Br-9-BBN solution (1.3 mmol, 1.0M in CH_2Cl_2) was added. A large amount of white precipitate formed immediately. This slurry was stirred for 3 hours at room temperature. Filtration and washing with hexanes (2x 1mL) and Et_2O (2x 1mL) yielded 0.463 g of

white solid, a 1:1 mixture of product and LiBr which ^{1}H NMR showed to include 4 equivalents of coordinated Et_2O. Overall yield: 65%. The product was then crystallized by cooling a saturated THF solution from room temperature to -22 °C over 4 days. ^{1}H NMR(CD_2Cl_2): 0.75 (t, 16H, $(CH_3CH_2)_2O$, $^3J_{HH}$ = 7.1 Hz), 1.32 (m, 4H, $B[(CH)_2(CH_2)_4(CH_2)_2,]$), 1.82 (m, 8H, $B[(CH)_2(CH_2)_4(CH_2)_2,]$), 1.98 (m, 2H, $B[(CH)_2(CH_2)_4(CH_2)_2]$), 2.25 (s, 6H, CH_3), 2.97 (t, 16H, $(CH_3CH_2)_2O$, $^3J_{HH}$ = 7.3 Hz), 6.98 (t, 2H, *H*Ar, $^3J_{HH}$ = 8.0 Hz) 7.09 (t, 2H, *H*Ar, $^3J_{HH}$ = 7.3 Hz), 7.42 (d, 2H, *H*Ar, $^3J_{HH}$ = 8.0 Hz), 7.54 (s, 2H, *H*Ar), 8.09 (d, 2H, *H*Ar, $^3J_{HH}$ = 8.6 Hz) ^{13}C NMR (C_6D_6): 9.69 (*C*Me), 25.80 ($O(CH_2)_2(CH_2)_2$), 40.66 (*C*H(3-methylindolyl)$_2$), 68.55 ($O(CH_2)_2(CH_2)_2$), 107.30 (*C*Ar), 115.13 (*C*Ar), 115.99 (*C*Ar), 117.66 (*C*Ar), 117.98 (*C*Ar), 119.83 (*C*Ar), 130.35 (*C*Ar), 131.54 (*C*Ar), 132.93 (*C*Ar), 146.89 (*C*Ar), 147.51 (*C*Ar), 147.69 (*C*Ar)

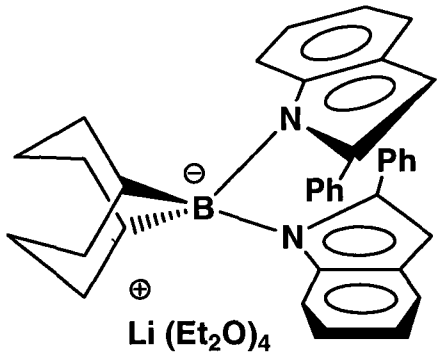


Attempted preparation of *Lithium(THF)$_4$ Di(2-methylindolyl)bicyclononylborate* **2.1** The procedure used in the synthesis of **1.15** was repeated substituting 2-methylindole (0.338g, 2.58 mmol) for 3-methylindole and THF for Et_2O. After addition of the Br-9-BBN reagent, the solution changed to a red/brown in colour. After stirring 4 hours, the THF was removed *in vacuo* to give red/brown oil, which was washed with 10mL toluene and filtered to yield 0.061g white solid and golden-orange solution. Overall yield: ^{1}H NMR ($CDCl_3$): 1.3 (m, 4H, $B[(CH)_2(CH_2)_4(CH_2)_2]$), 1.7 (q, 16H, $(CH_2CH_2)_2O$), 1.8 (m, 8H,

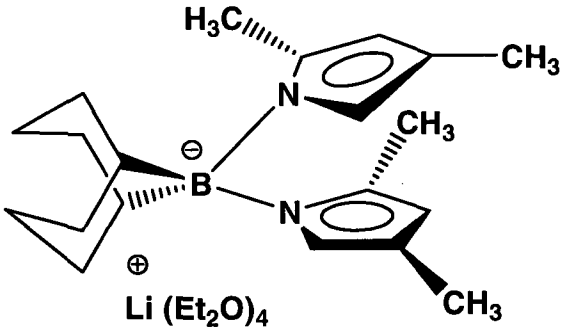
B[(CH)$_2$(CH_2)$_4$(CH$_2$)$_2$]), 1.8 (m, 2H, B[(CH)$_2$(CH$_2$)$_4$(CH$_2$)$_2$]), 2.6 (s, 6H, CH_3), 3.8 (t, 16H, (CH$_2$CH_2)$_2$O), 6.4 (t, 2H, *H*Ar) 7.7 (m, 6H, *H*Ar), 7.5 (m, 2H, *H*Ar), 7.6 (s, 2H, *H*Ar), 8.1 (d, 2H, *H*Ar)



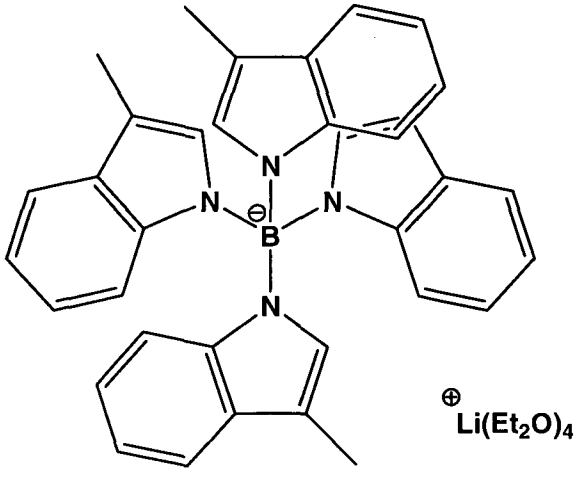
Attempted Preparation of *Lithium(Et$_2$O)$_4$ Bis(2-phenylindolyl)bicyclononylborate* **2.2** The procedure used in the synthesis of **1.15** was repeated substituting 2-phenylindole (0.500g, 2.59 mmol) for 3-methylindole. After addition of the Br-9-BBN reagent, the solution changed to a dark brown colour initially, but then reverted back to a clear yellow and gradually became dark orange. After stirring 48 hours, Et$_2$O was removed *in vacuo* to give red/brown oil which was washed with 3 mL hexanes and filtered to yield 0.128g of beige solid. ^{1}H NMR ($CDCl_3$): 1.3 (m, 4H, B[(CH)$_2$(CH$_2$)$_4$(CH_2)$_2$]), 1.5 (m, 8H, B[(CH)$_2$(CH_2)$_4$(CH$_2$)$_2$]), 1.5 (m, 4H, B[(CH)$_2$(CH$_2$)$_4$(CH_2)$_2$]), 1.8 (q, 16H, (CH_3CH$_2$)$_2$O), (s, 6H, CH_3), 2.97 (t, 16H, (CH$_3$CH_2)$_2$O), 6.8 (s, 2H, *H*Ar) 6.9 (s, 2H, *H*Ar), 7.2 (m, 2H, *H*Ar), 7.4 (m, 6H, *H*Ar), 7.6 (m, 4H, *H*Ar), 7.7 (m, 4H, *H*Ar), 7.8 (m, 2H, *H*Ar)



Attempted Preparation of *Lithium (Et_2O)$_4$ Bis(2,4-dimethylpyrrolyl)bicyclononylborate* **2.3** The procedure used in the synthesis of **1.15** was repeated substituting 2,4-dimethylpyrrole (0.50g, 5.3 mmol) for 3-methylindole and using 3.40 mL n-butyllithium solution (0.54 mmol, 1.6M in hexanes) After addition of the Br-9-BBN reagent, the solution turned orange. After stirring this reaction mixture for 24 hours the Et_2O was removed *in vacuo* to yield pink/beige oil which was washed with hexanes (1x 2mL) and Et_2O (2 x 2 mL) and placed under vacuum overnight to yield clumpy beige solid. ^{1}H NMR showed 2 products. The integration of the peaks corresponding to the indolyl methyl groups of each product indicated that they had formed in ~ 7:1 ratio. Major product: ^{1}H NMR ($CDCl_3$): 1.2 (m, 2H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 1.4 (m, 8H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 1.7 (m, 4H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 1.8 (q, 16H, $(CH_3CH_2)_2O$), 2.1 (s, 6H, CH_3), 2.4 (s, 6H, CH_3), 3.8 [t, 16H, $(CH_3CH_2)_2O$], 5.6 (s, 2H, *H*Ar) 6.9 (s, 2H, *H*Ar)



Attempted Preparation of *Lithium $(Et_2O)_4$ Tetrakis (3-methylindolyl)borate* **2.4** 0.200g 3-methylindole (1.52 mmol) was dissolved in 3 mL Et_2O in a vial. 0.96 mL n-butyllithium (1.5 mmol, 1.6M in hexanes) was added dropwise to this solution. The solution turned yellow and vigorous bubbling ensued immediately. After stirring for 3 hours 0.036 mL BBr_3 (0.37 mmol) was added. A large amount of white precipitate formed immediately. After the slurry was stirred for 4 hours the reaction mixture was suction filtered to give a white precipitate and a yellow solution. The white precipitate was insoluble in C_6D_6, $CDCl_3$; somewhat soluble in CD_2Cl_2. The solvent from the yellow solution was removed *in vacuo* to leave a yellow/orange oil. ^{1}H NMR(CD_2Cl_2): 1.27 (t, 16H, $(CH_3CH_2)_2O$), 2.36 (s, 6H, CH_3), 3.43 (t, 16H, $(CH_3CH_2)_2O$), 6.56 (m, 4H, *H*Ar) 6.94 (m, 4H, *H*Ar), 7.00 (m, 4H, *H*Ar), 7.17 (t, 4H, *H*Ar), 7.59 (t, 4H, *H*Ar)



Reactions of Lithium Bis(3-methylindolyl)bicyclononylborate

Lithium Bis(3-methylindolyl)bicyclononylborate + YCl_3: 0.162 g crystalline lithium bis(3-methylindolyl)bicyclononylborate (0.302 mmol) was dissolved in 2 mL THF to give a clear, colourless solution. 0.053g YCl_3 (0.271 mmol) was added to the solution, with stirring, to give a white slurry. After 1 day, the solution was now clear, colourless, with a small amount of colourless oily precipitate on the bottom. The solution was filtered from oily precipitate and the THF solvent was removed, leaving colourless oil. This oil was washed with hexanes (2 x 2 mL) and Et_2O (2 x 2 mL) and then dried *in vacuo* to give a white solid. ^{1}H NMR($CDCl_3$): 1.13 (m, 2H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 1.39 (m, 2H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 1.86 (m, 3H, $(CH_3CH_2)_2O$), 1.90 (broad m, 8H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 2.03 (broad m, 2H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 2.37 (s, 6H, CH_3), 3.92 (t, 3H, $(CH_2CH_2)_2O$], 7.01 (t, 2H, *H*Ar) 7.16 (t, 2H, *H*Ar), 7.22 (t, 2H, *H*Ar), 7.38 (d, 2H, *H*Ar), 7.62 (d, 2H, *H*Ar), 7.90 (s, 2H, *H*Ar)

Lithium Bis(3-methylindolyl)bicyclononylborate + $ZrCl_4$: 0.125 g crystalline lithium bis(3-methylindolyl)bicyclononylborate (0.233 mmol) was dissolved in 2 mL THF to give clear, colourless solution. 0.053g $ZrCl_4$ (0.227 mmol) was added to the solution, with stirring, which quickly turned to a yellow slurry. After 1 day, the solution was now clear and yellow. Hexanes (2 mL) were added, inducing an oily yellow precipitate. The remaining yellow solution was decanted from the precipitate, placed under vacuum to yield a yellow solid. ^{1}H NMR: 1.97 (m, 4H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 1.25 (m, 8H, $(CH_2CH_2)_2O$), 1.9-2.1 (broad m, 10H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 2.36 (s, 6H,

C*H*$_3$), 3.53 (t, 8H, (CH$_2$C*H*$_2$)$_2$O), 6.61 (s, H, *H*Ar) 7.00 (s, 2H, *H*Ar), 7.14 (t, 2H, *H*Ar), 7.21 (d, 2H, *H*Ar), 7.61 (m, 2H, *H*Ar), 7.90 (s, 1H, *H*Ar)

Lithium Bis(3-methylindolyl)bicyclononylborate + $TiCl_4(THF)_2$: 0.045 g crystalline lithium bis(3-methylindolyl)bicyclononylborate (0.117 mmol) was weighed into vial. 0.039g $TiCl_4(THF)_2$ (0.117 mmol) was added. 2 mL of toluene was then added to give a dark purple solution. After 1 day, the dark solution was filtered, though minimal solid was removed. Toluene was removed *in vacuo* to give an inhomogeneous mixture of yellow and purple solid. The ^{1}H NMR($CDCl_3$): 1.2-1.3 (m, 4H, B[(CH)$_2$(CH$_2$)$_4$(C*H*$_2$)$_2$]), 1.8-1.9 (m, 10H, B[(C*H*)$_2$(C*H*$_2$)$_4$(CH$_2$)$_2$]), 1.8 (m, 8H, (C*H*$_3$CH$_2$)$_2$O), 2.11 (s, 6H, C*H*$_3$), 3.9 (m, 8H, (CH$_2$C*H*$_2$)$_2$O), 7.0 (m, 6H, *H*Ar) 7.5 (d, 2H, *H*Ar), 7.8 (d, 2H, *H*Ar)

Lithium Bis(3-methylindolyl)bicyclononylborate + $CrCl_2(THF)_{1.3}$: 0.120 g crystalline lithium bis(3-methylindolyl)bicyclononylborate (0.224 mmol) was dissolved in 2 mL Et_2O to give a clear, colourless solution. 0.039 g $CrCl_2(THF)_{1.3}$ (0.180 mmol) was added to the solution, with stirring, to give grey slurry. Within 1 hour, the mixture had changed colour to maroon and then to deep turquoise with red precipitate. Red precipitate was then separated from the turquoise solution by filtration. The solvent was removed from the turquoise solution under vacuum to yield a turquoise solid. Dark green crystals were obtained by diffusion of hexanes into a saturated solution of the dark green solid redissolved in THF. Though products were anticipated to be paramagnetic, a ^{1}H NMR spectrum was taken and assignments predicted. ^{1}H NMR($CDCl_3$): 1.2 (broad s, 4H,

B[$(CH)_2(CH_2)_4(CH_2)_2$]),), 1.4(broad s, 10H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 2.3 (broad s, 6H, CH_3), 7.0 (broad s, 6H, *H*Ar) 7.3 (broad s, 2H, *H*Ar), 7.8-7.9 (broad s, 2H, *H*Ar)

Lithium Bis(3-methylindolyl)bicyclononylborate + $TaCl_5$: 0.235 g crystalline lithium bis(3-methylindolyl)bicyclononylborate (0.438 mmol) was dissolved in 2 mL THF to give a clear, colourless solution. 0.155g $TaCl_5$ (0.433 mmol) was added to the solution, with stirring, which quickly turned to reddish brown. After 1 day, the solution was now clear, yellow. 2mL hexanes were added, inducing an oily red precipitate and changing the remaining solution to a more yellowish-red colour. The yellow solution was separated from the red precipitate and placed under vacuum to yield a reddish-yellow solid. ^{1}H NMR: 1.29 (m, 4H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 1.88 (m, 8H, $(CH_3CH_2)_2O$), 1.9-2.1 (broad m, 10H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 2.37 (s, 6H, CH_3), 3.44 (t, 3H, $(CH_2CH_2)_2O$), 6.99 (t, 2H, *H*Ar) 7.13 (t of d, 2H, *H*Ar), 7.21 (t of d, 2H, *H*Ar), 7.37 (d, 2H, *H*Ar), 7.61 (d, 2H, *H*Ar)

Lithium Bis(3-methylindolyl)bicyclononylborate + $AlCl_3$: 0.100 g crystalline lithium bis(3-methylindolyl)bicyclononylborate (0.202 mmol) was dissolved in 2 mL Et_2O to give a clear, colourless solution. 0.027g $AlCl_3$ (0.205 mmol) was added to the solution. The mixture changed to a cloudy white. After 1 day, the solution was separated from a small amount of remaining solid by suction filtration and the solvent was removed *in vacuo*. The ^{1}H NMR spectrum showed resonances as follows: The ^{1}H NMR($CDCl_3$): 1.29 (m, 4H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 2.02 (m, 10H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 2.10 (m,

8H, ($CH_3CH_2)_2O$), 2.33 (s, 6H, CH_3), 7.2-7.3 (m, 4H, *H*Ar) 7.56 (d, 2H, *H*Ar), 7.88 (d, 2H, *H*Ar)

Lithium Bis(3-methylindolyl)bicyclononylborate + $CaCl_2$: 0.235 g crystalline lithium bis(3-methylindolyl)bicyclononylborate (0.438 mmol) was dissolved in 2 mL THF to give clear, colourless solution. 0.048 g $CaCl_2$ (0.432 mmol) was added to the solution, with stirring, to give a white suspension. After 1 day of stirring, the white slurry remained. The white solid was removed by suction filtration. 2mL of hexanes were added to the filtrate, inducing a white precipitate. The second white solid was removed by filtration to give gold solution. The solvent was removed *in vacuo* to give a pale red oil. ^{1}H NMR($CDCl_3$): 1.13 (m, 2H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 1.39 (m, 2H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 1.79 (m, 16H, ($CH_3CH_2)_2O$), 1.9-2.0 (broad m, 14H, B[$(CH)_2(CH_2)_4(CH_2)_2$]), 2.28 (s, 6H, CH_3), 3.53 (m, 16H, $(CH_2CH_2)_2O$), 6.9 (t, 2H, *H*Ar) 7.1 (m, 2H, *H*Ar), 7.4 (m, 2H, *H*Ar), 7.6 (m, 2H, *H*Ar), 8.1 (d, 2H, *H*Ar)

Synthesis of New Diindolylmethane Ligands

Di(3-methylindol-2-yl)-4-fluorophenylmethane **2.5** To a stirred solution of 1.00g (7.62 mmol) of 3-methylindole in 5 mL ethanol was added 0.473 g (3.81 mmol) 4-fluorobenzaldehyde. Ten drops of concentrated sulphuric acid were added to the solution and it was left to stir for 24 hours at room temperature. Volatiles were removed from the resulting dark blue solution by rotovap at reduced pressure to yield a dark blue solid. This solid was washed with hexanes (3 x 5 mL) and cold ethanol (3 x 5 mL) to yield 1.202 g **2.5** (85.6% yield). ^{1}H NMR(DMSO): δ 2.13 (s, 6H, 2 CH_3), 6.03 (s, 1H, C*H*(4-

bromophenyl)(3-methylindolyl)$_2$), 6.96 (t, 2H, *H*Ar, $^3J_{HH}$ = 7.6 Hz) 7.02 (t, 2H, *H*Ar, $^3J_{HH}$ = 7.5 Hz), 7.16 (d, 4H, *H*Ar, $^3J_{HH}$ = 7.4 Hz), 7.28 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.8 Hz), 7.43 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.6 Hz), 10.41 (s, 2H N*H*)

Di(3-methylindol-2-yl)-4-nitrophenylmethane **2.6** To a stirred solution of 1.00g (7.62 mmol) of 3-methylindole in 5 mL ethanol was added 0.576 g (3.81 mmol) 4-fluorobenzaldehyde. Ten drops of concentrated sulphuric acid were added to the solution and it was left to stir for 24 hours at room temperature. Volatiles were removed from the resulting brown solution by rotovap at reduced pressure to yield a light brown solid. This solid was washed with hexanes (3 x 5 mL) and cold ethanol (3 x 5 mL) to yield 1.018g dark blue solid **2.6** (67.6% yield) ^{1}H NMR (DMSO): δ 2.14 (s, 6H, 2 C*H*$_3$), 6.22 [s, 1H, C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 6.97 (t, 2H, *H*Ar, $^3J_{HH}$ = 7.8 Hz) 7.04 (t, 2H, *H*Ar, $^3J_{HH}$ = 7.4 Hz), 7.30 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.8 Hz), 7.43 (d, 2H, *H*Ar, $^3J_{HH}$ = 8.9 Hz), 8.22 (d, 2H, *H*Ar, $^3J_{HH}$ = 8.7 Hz), 10.47 (s, 2H N*H*)

Structural determination of 1

A single crystal was mounted on a thin glass fibre and held using viscous oil. It was subsequently cooled to the collection temperature. Crystal data and measurement details are summarized in **Tables 2.1** and **2.2**. Data was collected on a Bruker AX SMART 1k CCD diffractometer using 0.3o ω-scans at 0, 90 and 180 in ϕ. Unit-cell parameters were obtained from 60 frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied (Blessing, R. *Acta Cryst.* **1995**, *A51*, 33-38). Direct methods were used to solve molecular

structures and connectivity, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.1 program library (Sheldrick, G.M., Bruker AXS, Madison, WI, 1997).

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Chapter 3

Group 13 Complexes of a Diindolylmethane Ligand

I Diindolylmethane Chemistry of Main Group Elements

II Amido Complexes of Group 13 Elements

III Synthesis and Characterization of a Diindolylmethane Borane, Alane, and Possible Aluminum Alkyl

Group 13 Complexes of a Diindolylmethane Ligand

I Diindolylmethane Chemistry of Main Group Elements

Although many examples of diindolylmethane compounds can be found in the literature, the only fully structurally characterized coordination compounds of this class of molecules are four examples of titanium and zirconium amido complexes reported by Mason et. al.[1] Attempts toward diindolylmethane compounds of main group elements have been reviewed by Mason, and there are reported main group species in the literature.[2] The diindolylmethane framework imparts unique properties compared to other common chelating nitrogen-based ligands which have been used to bind to main group centres. Enhanced steric bulk and reduced Lewis acidity compared to many existing diamido ligands, as well as steric and electronic differences compared to the similar dipyrromethene framework demonstrate the potential to form main group complexes with reactivity distinct from existing coordination compounds. The chelate effect makes M-N-M bridging less likely and favours formation of N-heterocycles containing potentially reactive main group centres.[2] Here we present the first thoroughly characterized examples of Group 13 diindolylmethane structures.

II Amido Complexes of Group 13 Elements

There are many avenues of potential utility for Group 13 amido coordination compounds. High quantum yield dyes have been made with boron and aluminum complexes chelated by amido ligands, including the aforementioned dipyrromethene ligand used to support fluoroboranes to make the widely-used BODIPY dyes,[3] and dyes

using the related tetraminoperylene (TAP) ligand supporting both boron and aluminum hydrides.[4] The N-imidoylamidine ligand has been used to make cationic aluminum complexes,[5] while aluminum amidinates have been employed to synthesize mixed ligand complexes.[6] Extensive research is also being undertaken on various amine-boranes for hydrogen storage use.[7] Alkylaluminum compounds and aluminum hydrides have a wide range of uses as stoichiometric and catalytic reagents. Aluminum hydrides are good reducing agents and are precursors to several other classes of compounds including carbaalane[8,9] and amidoalane[10] clusters, alumoxane reagents,[11] aluminum chalcogenides,[12-16] aluminum-containing heterocycles,[17] and co-catalysts, the most well-known being MAO, for a number of polymerization reactions.[18, 19]

It is possible to envision a wide range of Group 13 coordination complexes of diindolylmethane. As diindolylmethane is a formally -2 ligand occupying two coordination sites, neutral complexes would feature an additional -1 substituent. Three-coordinate group 13 centres, especially the metalloids boron and aluminum, have well-documented Lewis acid properties due to electronic and coordinative unsaturation. Therefore, it was decided to focus on boron and aluminum as initial targets. Because diindolylmethane is anticipated to be a poorer donor than amido ligands featuring non-aromatic nitrogen atoms, diindolylmethane complexes of Group 13 atoms may be even more Lewis acidic, with minimal π-donation into the empty orbitals of the Group 13 atom. The unoccupied p-orbital of the atom opens up the possibility of π-donation from the third substituent of the Group 13 centre, or hyper-conjugation if lone pairs are available. The possibility of coordination of a neutral, dative donor at a fourth

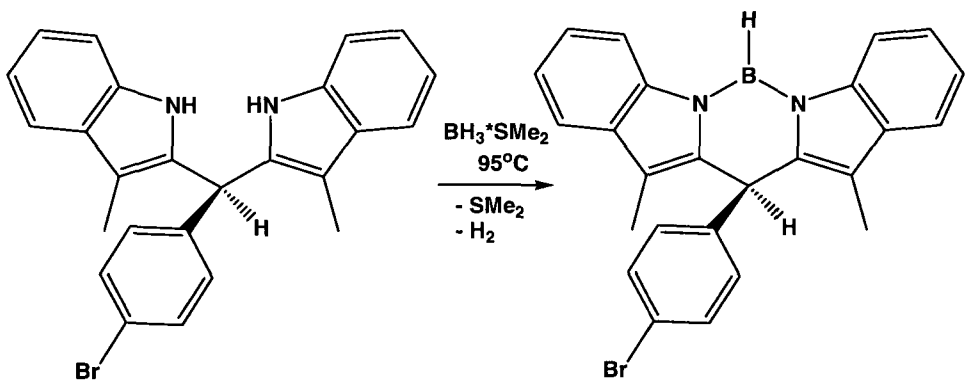
coordination site to fill the octet of the Group 13 atom offers further potential for variation of complexes and quenching of the Lewis acidity.

Dinuclear, bridging Group 13 compounds have also been documented, particularly alkyl aluminum species.[20,21] Sterics permitting, bridging interactions may be favoured as a means to achieve more electron density at the metalloid centre, or could be the result of using common Group 13 reagents such as $AlMe_3$ and BH_3 which exist as dinuclear species unless ligated with a dative donor. Therefore, the possibility of forming dinuclear species or even polynuclear clusters in reactions between Group 13 reagents and diindolylmethane was considered, even though the reactions targeted 1:1 stoichiometric ratios between diindolylmethane and the Group 13 reagents.

III Synthesis and Characterization of a Diindolylmethane Borane, Alane, and Possible Aluminum Alkyl

Diindolylmethane possesses two reactive protons of the indolyl nitrogen centers. Borane and alane starting materials are susceptible to reaction with these protons to undergo hydrogen elimination reactions and lead to incorporation of diindolylmethane ligands on the B and Al centers, respectively. Though borane-THF adducts have been used in similar hydrogen elimination reactions in some cases, reports of these adducts proving unreactive deterred us from using them as reagents.[20] The borane-dimethylsulfide adduct was instead employed. Reaction of borane-dimethylsulfide with diindolylmethane in toluene at 95°C for 24 hours according to **Scheme 3.1** resulted in initial formation a clear, yellow solution. It was clear by the disappearance of the di(3-methylindol-2-yl)-4-bromophenylmethane reagent, insoluble in toluene, that a reaction

was proceeding. Removal of volatiles and crystallization of the resultant solid by slow diffusion of n-hexanes into a solution of the product in toluene gave crystals of **3.1** in fair yield. It was possible to obtain the product pure as determined by ^{1}H NMR in very high yield. ^{1}H and ^{13}C NMR spectra for this species show the expected signals with resonances shifted somewhat from the free ligand and the NH protons absent from the ^{1}H NMR spectra. A single broad resonance can be discerned for the proton bonded to the boron atom of **3.1**. A ^{11}B NMR spectrum showed one signal at about 23 ppm.



3.1

Scheme 3.1: Synthesis of **3.1**

The structure of **3.1** was confirmed by X-ray crystallography with the results summarized in **Tables 3.1** and **3.2** and **Figure 3.1**. The structure shown in **Figure 3.1** demonstrates that complex **1** displays a slightly-distorted trigonal planar boron centre. The N-B-N angle is slightly smaller than the H-B-N angles, indicating that the slight distortion is likely caused by the rigidity of the ligand. Though the H-B-N angles could not be confirmed using X-ray diffraction, it is apparent that the H-B-N angles are >120° since the N-B-N angle is < 120°; H-B-N angles listed in **Table 1** were estimated using Mercury.[21] The dimethylsulfide coordinated to the borane starting material was absent in

the NMR spectra of the product and its absence is further confirmed with the X-ray structure. Presumably the Me_2S dissociated during reaction and was removed from the reaction mixture when it was placed under vacuum to remove the solvent.

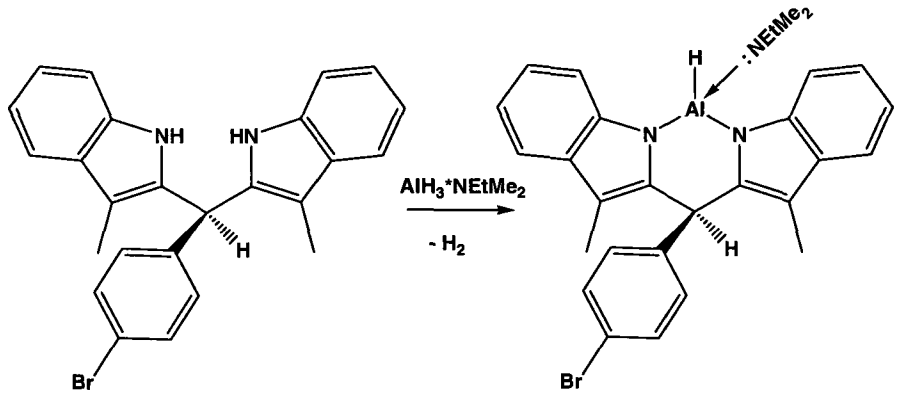
The solid-state structure of **3.1** shows B-N bond lengths of 1.417(10) Å and 1.422(10)Å, nearly the same as the bond lengths of 1.413(3)Å and 1.418(3)Å measured for the solid-state structure of an analogous diaminonaphthalene borane.[20] It was expected that the B-N bonds of **3.1** would be significantly longer than those of the diaminonaphthalene borane due to the aromaticity of the indolyl nitrogen lone pair inhibiting π-donation compared to the non-aromatic nitrogen lone pair of diaminonaphthalene. The resultant difference in electron density was expected to manifest itself as longer B-N bonds in **3.1**. The difference in bond lengths between the two borane complexes was perhaps expected to be even more pronounced than for E-N bonds between non-boron complexes of these ligands, as boron has an empty p-orbital to facilitate π-donation as well and is as in the same row of the periodic table as nitrogen, favouring greater orbital overlap.

A slight deviation from planarity in the six-membered heterocycle formed by bidentate coordination to boron is observed. The plane of the 4-bromophenyl ring is nearly perpendicular to the plane of the two indole moieties.

Formation of the analogous alane complex as shown in **Scheme 3.2** was even more kinetically favourable than formation of **3.1**, as reaction of alane-dimethylethylamine complex and diindolylmethane in toluene yielded product **3.2** in high yield at room temperature within one hour. Like the synthesis of **3.1**, it was apparent that the reaction was proceeding as the insoluble white di(3-methylindol-2-yl)-4-

bromophenylmethane disappeared. The product **3.2** was a white solid. ^{1}H and ^{13}C NMR spectra show the expected signals; resonances are distinct from those of the free ligand and the NH protons are absent from the ^{1}H NMR spectra. The aluminum hydride resonance was not visible in the ^{1}H NMR spectrum due to the quadrupolar coupling of the aluminum nucleus to the proton. The ^{1}H NMR shifts are also somewhat shifted in comparison to **3.1,** and the diagnostic methyl and methylene proton signals are both shifted significantly (>+/- 0.5ppm) from the spectrum of **3.1**.

Signals in the ^{1}H NMR spectrum of **3.2** corresponding to ethyldimethylamine, the stabilizing adduct in the alane reagent, were visible and integrated for roughly one equivalent of amine per molecule. This is in contrast to the dimethylsulfide stabilizing adduct in the borane starting materials which was absent from the final product **3.1**. Because the boiling points for each of these adduct compounds are nearly identical when they are uncoordinated (36°C for ethyldimethylamine, 37°C for dimethylsulfide) and because the reaction and work-up conditions for both the borane and alane syntheses were similar, it is reasonable to conclude that the presence of the amine alkyl resonances in the NMR spectrum of **3.2** indicate that it is coordinated to the aluminum in the final product. This is consistent with observations of other amino alane complexes synthesized using the same reagent.[4, 17, 20]

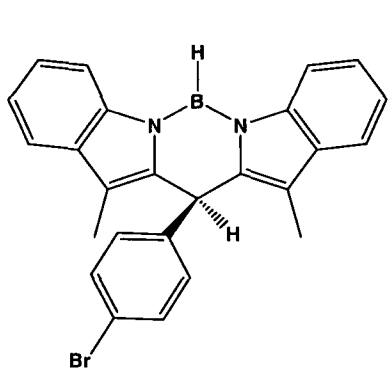


3.2

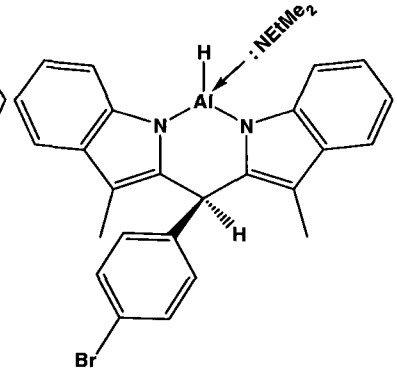
Scheme 3.2: Synthesis of **3.2**

An analogous proton transfer reaction between diindolylmethane and trimethylaluminum was also explored. This reaction was conducted in toluene at both room and elevated temperature and did proceed as evidenced by disappearance of di(3-methylindol-2-yl)-4-bromophenylmethane, insoluble in toluene, to give a clear, yellow solution. ^{1}H NMR analysis showed this reaction was decidedly less clean than the reactions of the borane and alane with diindolylmethane, though it yielded a major product postulated to be **3.3** based on ^{1}H NMR analysis and the demonstrated propensity of trimethylaluminum, a dinuclear reagent, to form dinuclear complexes in reactions with bidentate nitrogen ligands.[22] Signals at low field (-0.4ppm, -1.3ppm) in the ^{1}H NMR spectrum likely corresponding to the methyl groups attached to the aluminum centres were discerned but were broad and when it was attempted to integrate them they did not appear to account for twelve methyl protons expected if the product were indeed **3.3**. However, the integration appeared to account for significantly more than the three protons expected for a mononuclear species. A mononuclear species bonded to only one of the nitrogen atoms, representing incomplete reaction of the ligand, was discounted as a

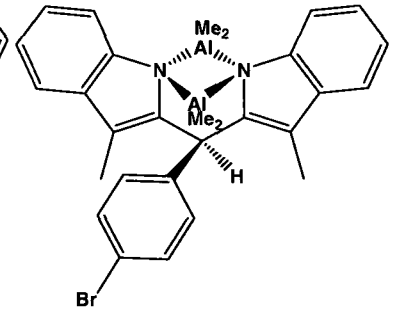
possibility as it was clear from the ^{1}H NMR spectrum that both NH protons were absent and that the product had retained the symmetry of the ligand. Therefore, given the proof of analogous reactivity the diaminonaphthalene ligand has shown with Group 13 species, it is postulated that the product from the reaction is **3.3**. Further characterization is ongoing,



3.1



3.2



3.3

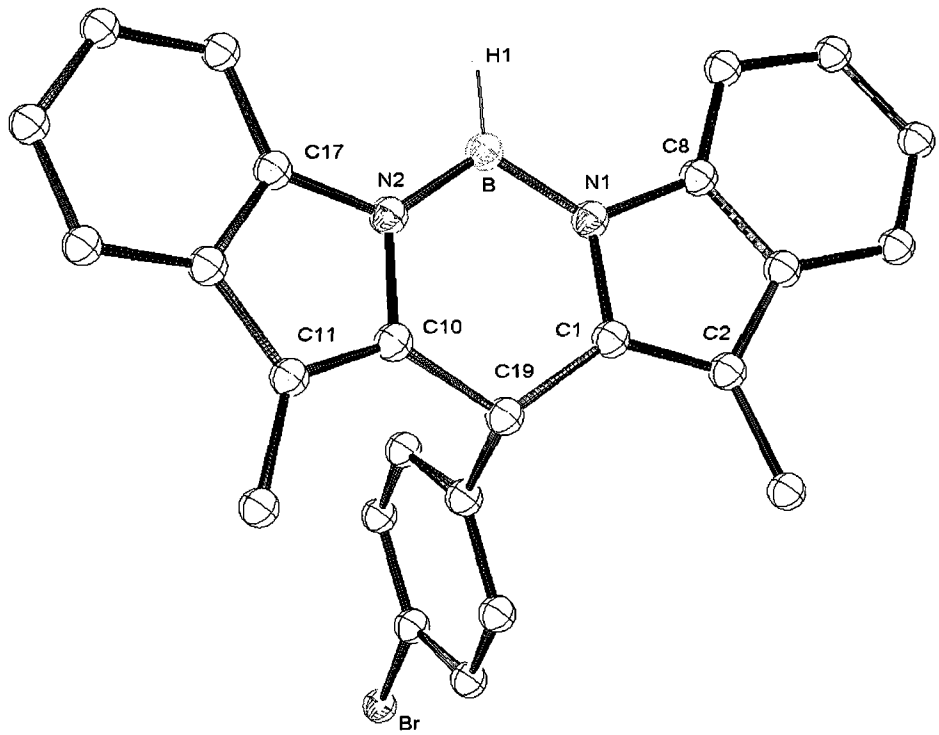


Figure 3.1: Solid-state structure of and atomic numbering scheme of **3.1**. Thermal ellipsoids are drawn at 30% probability.

Table 3.1 Selected Bond Lengths (Å) and Angles (deg) for 3.1

A	B	Distance	A	B	C	Angle
B	N1	1.417(10)	B	N1	N2	115.8(6)
B	N2	1.422(10)	H1	B	N1	122.7*
N1	C1	1.402(8)	H1	B	N2	121.5*
N1	C8	1.403(8)	B	N1	C1	124.5(6)
N2	C10	1.420(9)	B	N1	C8	128.1(6)
N2	C17	1.404(8)	B	N2	C10	125.3(6)
			B	N2	C17	128.8(6)

*H-B-N angles were estimated using Mercury

Table 3.2 Selected Crystal Data and Collection Parameters for **3.1**

empirical formula	C_{25} H_{20} B Br N_2
formula weight	439.15
T (K)	203K
λ(Å)	0.71073
crystal system	monoclinic
space group	P 2_1/c
a (Å)	11.179(2)
b (Å)	21.713(4)
c (Å)	8.9530(16)
α (deg)	90
β (deg)	90
γ (deg)	113.350(2)
V (Å^3)	1995(18)
Z	4
Abs. coeff. (mm-1)	2.074 mm^{-1}
Final R indices	R1 = 0.0834
	wR2 = 0.2146()

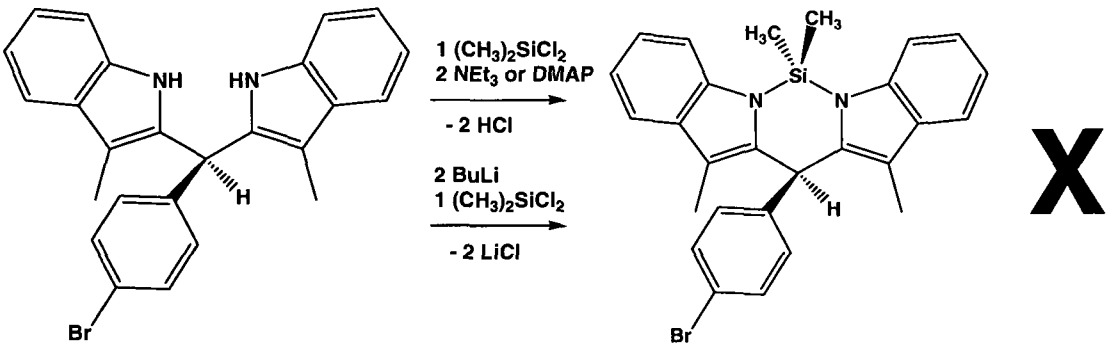
IV Foray Into Group 14

Two examples of diindolylmethane diphenylsilane complexes are cited in a 2003 review[2] as pending publication, but we have not been able to verify that they have since been published. Therefore, no experimental or characterization data are available on these compounds. To the best of our knowledge, no other Group 14 diindolylmethane compounds exist in the literature. However, the fact that silane compounds were mentioned in the review indicated that Group 14 chemistry of diindolylmethanes might be a promising avenue to explore.

Carbazoles, which are a variation of indoles with a second benzene ring fused to the 2-3 position of the pyrrole moiety, have ligated a variety of silane complexes.[23] Salt metathesis reactions between the lithium or potassium salts of carbazole and $SiCl_4$ were

the primary methods used to synthesize these complexes.[23] In addition, germanium complexes have been synthesized supported by a diamidonaphthalene ligand.[24] Thus, there is precedent for similar aromatic and non-aromatic nitrogen donor ligands chelating to Group 14 centres.

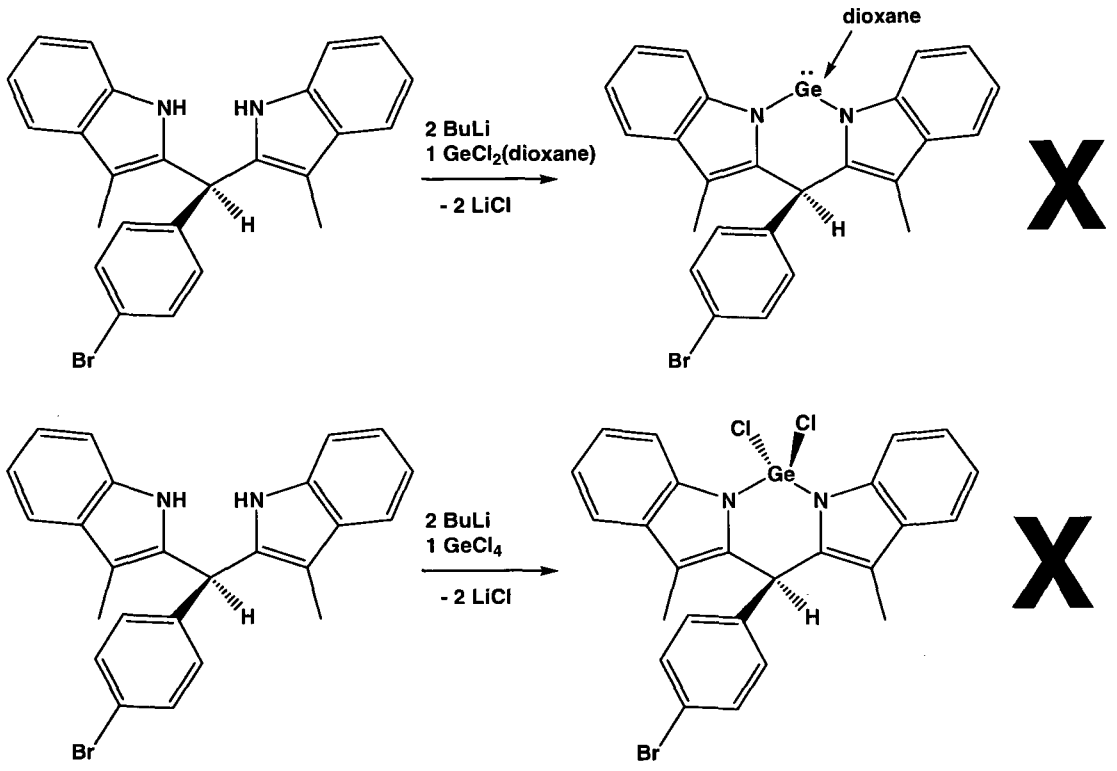
It was decided to attempt to form a dimethylsilane diindolylmethane complex **3.4** using dichlorodimethylsilane as a starting material. This reagent allowed us the breadth to employ multiple synthetic strategies to attempt to displace the chlorine atoms with diindolylmethane, including salt metathesis and dehydrohalide coupling according to **Scheme 3.3**, with a number of different reagents. Dehydrohalide coupling reactions, using either triethylamine (NEt_3) or dimethylaminopyridine (DMAP) as base "scavengers" to neutralize the HCl evolved in the reaction of the di(3-methylindol-2-yl)-4-bromophenylmethane ligand with dichlorodimethylsilane proved unsuccessful. ^1H NMR studies indicated an intractable mixture of products formed. Salt metathesis reactions involving lithiation of the ligand with n-butyllithium followed by reaction with dichlorodimethylsilane initially appeared to be a more promising avenue of investigation. ^1H NMR spectra indicated four distinct products formed, evidenced by four distinct resonances for the both the diagnostic indolyl methyl groups and for the methylene proton at the carbon bridging the two indole moieties. Integration of these resonances demonstrated that these four products accounted for approximately 40%, 30%, 20% and 10% of the overall mixture, respectively. The lithium salt of the ligand was found to be the product accounting for 20% of the mixture. Further studies on this species are discussed in the next chapter of this report. Inability to separate the products of the reaction made it impossible to further characterize the remaining products.



3.4

Scheme 3.3 Attempted syntheses of a di(3-methylindol-2-yl)-4-bromophenylmethane dimethylsilane complex **3.4**

Analogous reactions employing both Ge(IV) and Ge(II) reagents were met with a similar lack of success in attempts to form Ge(II) **3.5** and Ge(IV) **3.6** complexes of di(3-methylindol-2-yl)-4-bromophenylmethane. $GeCl_4$ and the dioxane adduct of $GeCl_2$ were employed and appeared to react with the lithiated ligand but the products formed were extremely insoluble, precipitating from THF solutions. Insolubility precluded most efforts at characterization, as solution-state NMR was impossible due to the fact that common NMR solvents could not be used; analysis by single-crystal X-ray diffraction could not be carried out because crystals could not be grown without dissolving sufficient product. The products also proved to be air and moisture-sensitive. Removal from dry atmosphere and solvent in an attempt at dissolution in deuterated DMSO resulted in re-protonation of the ligand, which proved to be the only species visible in the ^1H NMR spectrum. It appears that successful isolation of Group 14 diindolylmethane species, while remaining an attractive target, must be attained using other methods.



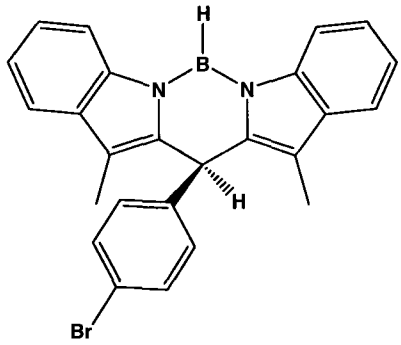
Scheme 3.4 Attempted syntheses of germanium (II) and germanium (IV) complexes of Di(3-methylindol-2-yl)bromophenylmethane

Experimental Section

General Considerations All manipulations were carried out under nitrogen employing standard drybox techniques. All solvents were sparged with nitrogen and dried by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Deuterated benzene was dried by addition of molecular sieves. Di-(3-methylindol-2-yl)-4-bromophenylmethane was prepared according to a previously reported procedure.[25] $GeCl_2$(dioxane) was prepared according to a previously reported procedure.[26] All other reagents were purchased from Aldrich and used as received. NMR spectra were run on Bruker Avance 300 and 500 MHz spectrometers with deuterated benzene as the solvent using residual protons of the deuterated solvent for reference. Element analysis was performed by Mr. Titel Jurca at the Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, ON.

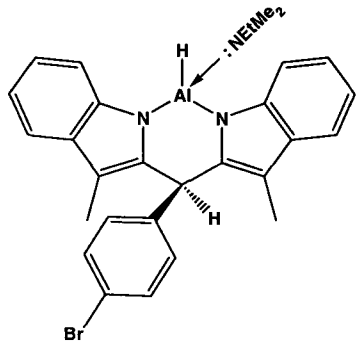
Di-(3-methylindol-2-yl)borane-4-bromophenylmethane **3.1** To a suspension of 0.100g di-(3-methylindolyl)-4-bromophenylmethane (0.233 mmoles) in toluene was added 0.120 mL BH_3*$S(CH_3)_2$ (0.240 mmoles, 2.0M solution in toluene) at room temperature. The reaction mixture was then heated to 90° C for 24 hours to yield a clear, yellow solution. The solvent was then removed in vacuo to yield a yellow solid, which was washed with n-hexanes (3 x 1.5 mL) and diethyl ether (3 x 1.5 mL) to yield white solid **3.1** in 86.4% yield. Colourless crystals were obtained when hexanes were diffused into a toluene solution of **3.1** cooled to -22 C° overnight. ^{1}H NMR(C_6D_6): δ 1.90 (s, 6H, 2 C*H*$_3$), 5.24 [s, 1H, C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 6.62 (d, 2H, *H*Ar $^3J_{HH}$ = 8.1 Hz) 7.04 (d, 2H, *H*Ar $^3J_{HH}$ = 8.2 Hz), 7.29 (m, 4H, *H*Ar $^3J_{HH}$ = 5.3 Hz), 7.40 (d, 2H, *H*Ar $^3J_{HH}$ = 6.5 Hz),

7.75 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.3 Hz) ^{13}C NMR (C_6D_6): δ 8.90 (*C*Me), 40.04 (*C*H(3-methylindolyl)$_2$), 42.34, 112.43 (*C*Ar), 115.11 (*C*Ar), 118.97 (*C*Ar), 120.66 (*C*Ar), 123.12 (*C*Ar), 123.77 (*C*Ar), 129.42 (*C*Ar), 132.28 (*C*Ar), 133.52 (*C*Ar), 134.65 (*C*Ar), 139.82 (*C*Ar), 142.23 (*C*Ar)) ^{11}B NMR (C_6D_6): δ 23 ppm (B) Anal. Calcd. For $C_{25}H_{20}BBrN_2$: C 68.37 H 4.59, N 6.38 Found: C 68.18 H 4.59 N 6.19



Di-(3-methylindol-2-yl)alane-4-bromophenylmethane **3.2** To a suspension of 0.100g di-(3-methylindolyl)-4-bromophenylmethane (0.233 mmoles) in toluene was added 0.240mL AlH_3*$N(CH_3)_2CH_2CH_3$ (0.240 mmoles, 1.0M solution in toluene) at room temperature. Within 5 minutes, the reaction mixture became a clear, colourless solution. After approximately one hour, white solid precipitated from this mixture. The solid was separated from the solution by suction filtration and washed with n-hexanes (2 x 1.5 mL) to yield 0.120g of white solid **3.2**. **Yield**: 95% ^{1}H NMR(C_6D_6): δ 0.06 (t, 3H, NCH_2CH_3), 1.36 (s, 6H, NCH_3), 1.87 (q, 2H, NCH_2CH_3), 2.41 (s, 6H, 2 CH_3), 5.92 [s, 1H *C*H(4-bromophenyl)(3-methylindolyl)$_2$], 6.81 (d, 2H, *H*Ar, $^3J_{HH}$ = 8.4 Hz) 7.07 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.8 Hz), 7.37 (m, 4H, *H*Ar, $^3J_{HH}$ = 7.5 Hz), 7.51 (m, 2H, *H*Ar, $^3J_{HH}$ = 8.4 Hz), 7.81 (m, 2H, *H*Ar, $^3J_{HH}$ = 6.9 Hz) Al*H* resonance was not observed in ^{1}H NMR spectrum due to broadening of signal from coupling to quadrupolar Al nucleus. ^{13}C NMR (C_6D_6): δ 6.59 (*C*Me), 9.65 (NCH_2CH_3), 39.57 (*C*H(3-methylindolyl)$_2$), 42.34 (NCH_3), 52.05

(NCH_2CH_3), 112.19 (*C*Ar), 113.44 (*C*Ar), 119.40 (*C*Ar), 119.89 (*C*Ar), 120.57 (*C*Ar), 121.59 (*C*Ar), 130.36 (*C*Ar), 132.00 (*C*Ar), 132.87 (*C*Ar), 140.83 (*C*Ar), 143.01 (*C*Ar), 144.01 (*C*Ar)



Di-(3-methylindol-2-yl)methylaluminum-4-bromophenylmethane **3.3** 0.24mL (0.240 mmol) $AlMe_3$ was added to suspension of 0.100g di-(3-methylindolyl)-4-bromophenylmethane (0.233 mmol) in toluene at room temperature. The reaction mixture was then heated to 90° C overnight. After 24 hours, volatiles were removed and the resulting solid was washed with n-hexanes (2 x 1.5 mL) to yield an off-white solid. This solid was washed with Et_2O (2 x 0.5mL) and re-precipitated from toluene to yield 0.080 g of off-white solid hypothesized to be **3.3**. **Yield:** 68.2% ^{1}H NMR(C_6D_6):δ -1.3 (s, 3H, C*H*$_3$), -0.4 (s, 3H, C*H*$_3$), 0.2 (m, 3H, C*H*$_3$), 0.9 (m, 3H, CH*3*), 1.66 (s, 6H, 2 C*H*$_3$), 5.83 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 6.99 (d, 4H, *H*Ar, $^3J_{HH}$ = 8.4 Hz) 7.20 (m, 4H, *H*Ar, $^3J_{HH}$ = 8.7 Hz), 7.36 (m, 2H, *H*Ar, $^3J_{HH}$ = 8.7 Hz), 7.89 (m, 2H, *H*Ar, $^3J_{HH}$ = 5.4 Hz)

Attempted Preparation of *Di-(3-methylindol-2-yl)dichlorosilane-4-bromophenylmethane* **3.4**: To a solution of 0.214g di-(3-methylindolyl)-4-bromophenylmethane (0.500 mmoles) in THF was added 0.64 mL n-BuLi (1.00 mmoles, 1.6M solution in hexanes) at room

temperature. Immediate bubbling ensued with concomitant colour change to golden yellow and then within minutes to purple. After allowing to stir for 1 hour, 0.060 mL $(CH_3)_2SiCl_2$ (0.030g, 0.50 mmol) was added. The reaction was carried out at both room temperature and 65°C for times between 2 and 48 hours; resulted in brown slurry. The solid was filtered off and ^{1}H NMR analysis showed only solvent peaks. Volatiles from the filtrate were removed in vacuo to yield dark green oil oil. Washing with hexanes (2 x 2mL) yielded 0.085g of a lime-green powder. If this was desired product, yield would be 35%. ^{1}H NMR (major product, C_6D_6): δ 2.28 (s, 6H, 2 C*H*$_3$), 5.92 [s, 1H, C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 6.63 (d, 2H, *H*Ar) 6.96 (m, 4H, *H*Ar), 7.23 (m, 4H, *H*Ar), 7.65 (d, 2H, *H*Ar)

Attempted Preparation of *Di-(3-methylindol-2-yl)germanium-4-bromophenylmethane* **3.5**: To a solution of 0.100g di-(3-methylindolyl)-4-bromophenylmethane (0.233 mmoles) in THF was added 0.30 mL n-BuLi (0.47 mmoles, 1.6M solution in hexanes) at room temperature. Immediate bubbling ensued with concomitant colour change to golden yellow and then within minutes to purple. After allowing to stir for 1 hour, 0.054g $GeCl_2$(dioxane) (0.50 mmol) was added. After an additional hour stirring, the reaction mixture had become a yellow slurry. The yellow precipitate was removed by filtration and the mass was measured as 0.088g. The filtrate was placed under vacuum but very little material remained after solvent was removed. If yellow precipitate was desired product, yield would be 75%. ^{1}H NMR analysis on the yellow solid was impossible due to insolubility.

Attempted Preparation of *Di-(3-methylindol-2-yl)germaniumdichloride-4-bromophenylmethane* **3.6**: To a solution of 0.188g di-(3-methylindolyl)-4-bromophenylmethane (0.44 mmoles) in THF was added 0.55 mL n-BuLi (0.88 mmoles, 1.6M solution in hexanes) at room temperature. Immediate bubbling ensued with concomitant colour change to golden yellow and then within minutes to purple. After allowing to stir for 1 hour, 0.050 mL $GeCl_4$ (0.094g, 0.44 mmol) was added. The solution gradually became a deep yellow slurry. After 24 hours stirring, the yellow precipitate was removed by filtration and the mass was measured as 0.170g. The filtrate was placed under vacuum but very little material remained after solvent was removed. If yellow precipitate was intended product, yield would have been 68%. ^{1}H NMR analysis on the yellow solid was impossible due to insolubility.

Structural determination of 3.1

A single crystal was mounted on a thin glass fibre and held using viscous oil. It was subsequently cooled to the collection temperature. Crystal data and measurement details are summarized in **Tables 2.1** and **2.2**. Data was collected on a Bruker AX SMART 1k CCD diffractometer using 0.3o ω-scans at 0, 90 and 180 in ϕ. Unit-cell parameters were obtained from 60 frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied (Blessing, R. *Acta Cryst.* **1995**, *A51*, 33-38). Direct methods were used to solve molecular structures and connectivity, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are

contained in the SHELXTL 5.1 program library (Sheldrick, G.M., Bruker AXS, Madison, WI, 1997).

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Chapter 4

Diindolylmethane Complexes of the s-Block Metals

I s-Block Metal Amido Complexes

II Catalysis with s-Block Metal Compounds

III Synthesis of Reactive Dinuclear s-Metal Complexes of Diindolylmethane

IV Synthesis of Ca[di(3-methylindolyl)-4-bromophenylmethane*$(THF)_4$]

Diindolylmethane Complexes of the s-Block Metals

I s-Block Metal Amido Complexes

Amido compounds of s-block metals have found utility as precursors in the synthesis of both transition metal and main group targets and have demonstrated catalytic activity themselves.[1a-j] Salt metathesis reactions involving reaction of metal halides with anionic carbon and nitrogen centres metallated with a group 1 or 2 metal are a well-established and simple way of installing nitrogen onto transition and main-group metals. As it is only recently that diindolylmethane compounds have been re-examined for use as bidentate ligands,[2] this methodology has yet to be employed to generate new main group coordination complexes of this ligand. There are only two reported transition metal diindolylmethane compounds generated by salt metathesis; in these reactions, butyllithium was added to deprotonate the ligand and titanium and zirconium halides were added in situ.[3] The intermediate lithium salt was not reported isolated or characterized. Indeed, reported coordination chemistry of diindolylmethane ligands has been restricted to a small number of Group 4[4] and Group 13 and 14 complexes,[5] with some of these incompletely characterized. To the best of our knowledge, no diindolylmethane compounds of s-block metals have been reported.

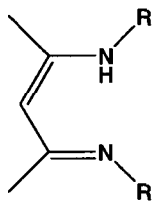
II Catalysis With s-Block Metal Compounds

Traditionally, more attention has focused on synthesis of transition-metal than main group complexes for catalysis. However, in the last few years there has been increasing interest in the potential catalytic applications of main group complexes,

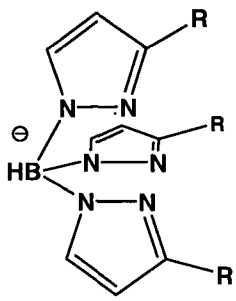
including the s-block metals. Catalytic applications have been found for many readily-available reagents traditionally used stoichiometrically such as butyl lithium,[6] 1-hexynyllithium,[7] lithium dimethylamide (LDA)[1a, 8] and alkali-metal alkoxides of lithium, sodium, potassium and rubidium.[1h,1i,1j] More complex alkali-amido molecules than LDA have also found uses catalytically, such as diamidobinaphthyldilithium complexes for asymmetric hydroamination/cyclization reactions.[1b] The alkaline earth metals have perhaps even more catalytic diversity, particularly magnesium and calcium. Among molecules featuring nitrogen-based ligands, hydroamination[1d] and hydrophosphination[9] reactions facilitated by calcium β-diketiminato complexes are known. Magnesium and calcium complexes have also been found to polymerize a variety of useful substrates, most notably styrene[1c] and lactide.[1e,10-12] Lactide polymerization in particular is an attractive end for which calcium catalysts have proven to be a means, as polylactides are biodegradable, biocompatible polymers which can be used as a bulk packaging material. The synthesis of biodegradable packaging materials is a developing front of green chemistry which is increasingly commercially important.[13]

β-diiminate[1e,10-12] and poly-pyrazolylborate[1e] complexes in particular have proven effective catalysts for lactide polymerization. The magnesium β-diiminate catalysts and calcium tris-pyrazolylborate catalysts have exhibited stereoselectivity, forming heterotactic polylactides, while the calcium β-diiminate catalysts have yielded atactic polylactides.[1e,10-12] The diindolylmethane ligand has obvious structural similarities to β-diiminate **4.1** and poly-pyrazolylborate ligands **4.2, 4.3**; potential diindolylmethane coordination complexes would feature a pair of chelating nitrogen atoms forming a 6-membered heterocycle with the metal to which they are ligated, just as

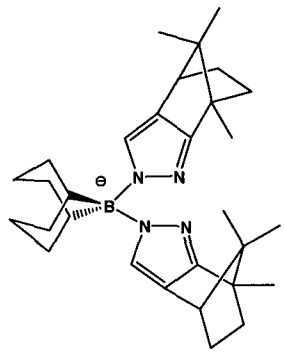
the β-diiminiate and bis-pyrazolylborate complexes do. These similarities highlight the potential for Group II complexes of diindolylmethane to exhibited similar catalytic activity.



4.1



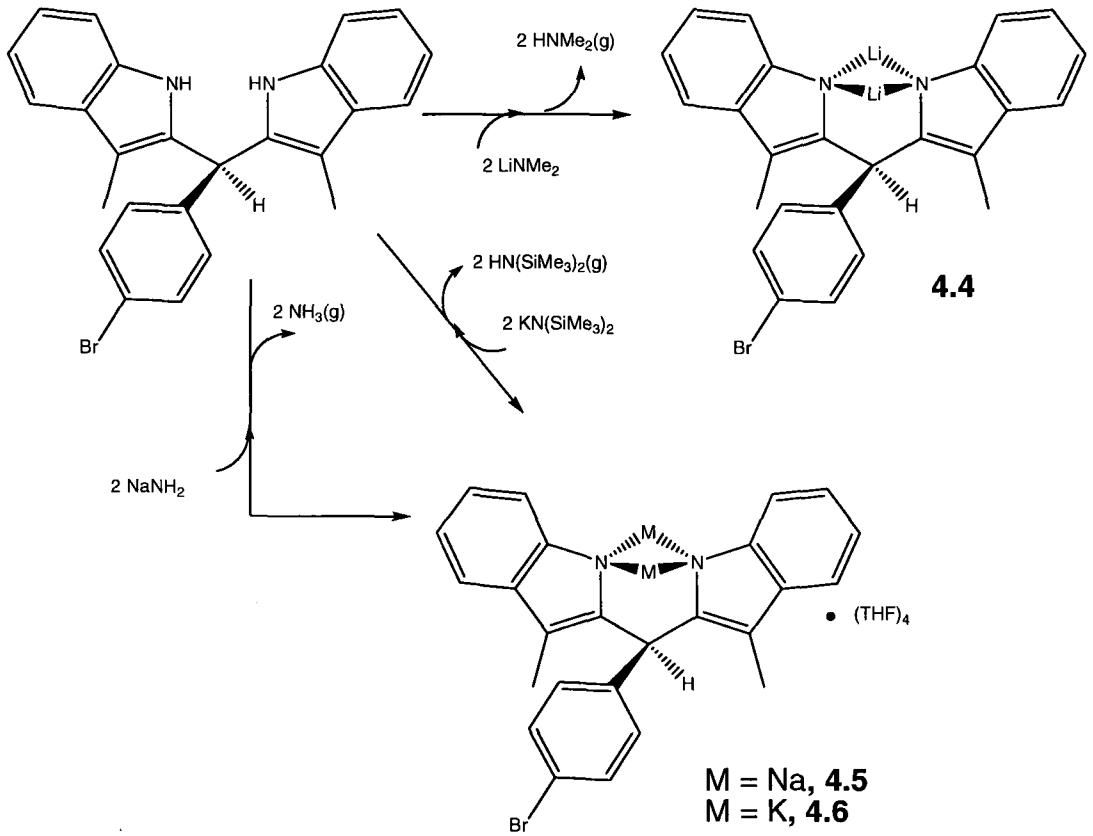
4.2



4.3

III Synthesis of Reactive Dinuclear s-Metal Complexes of Diindolylmethane

The N-H functions of di(3-methylindol-2-yl)-4-bromophenylmethane react with 2 equivalents of n-butyllithium or $Li[N(CH_3)_2]$ in THF or Et_2O with accompanying evolution of butane or dimethylamine gas, respectively, and a rapid change from colourless to yellow to purple to yield a quantitative transformation to the lithium salt **4.4** within 2 hours (**Scheme 4.1**). Compound **4.4** was isolated as both a THF and an Et_2O adduct as indicated by the ^1H and ^{13}C NMR spectra which displayed the resonances for the diindolylmethanide ligand dianion along with four equivalents of OC_4H_8 or OC_4H_{10}.



Scheme 4.1: Syntheses of dimetallic Group 1 diindolylmethane salts. Coordinating solvent molecules are omitted from the structures **4.4, 4.5** and **4.6** for clarity.

An analogous reaction of di(3-methylindol-2-yl)-4-bromophenylmethane with 2 equivalents of $NaNH_2$ in THF gave a yellow solution and also resulted in quantitative transformation by NMR to the sodiated ligand **4.5** within 2 hours. As with compound **4.4**, the ^1H NMR spectrum of **4.5** showed THF in the product, in this case 4 equivalents. Similarly, reaction of 2 equivalents of $K\{[N[Si(CH_3)_3]_2\}$ with di(3-methylindol-2-yl)-4-bromophenylmethane in THF yielded a solid presumed to be the related compound **4.6**. Unfortunately, this material proved to be insoluble in common NMR solvents which prohibited more definitive characterization. Compound **4.4** ,**4.5** and **4.6** all proved reactive with metal halides MX_n (M= Al, Ca).

Crystals suitable for single crystal X-ray analysis were obtained by recrystallizing compound **4.4** from diethyl ether. The results of this analysis are presented in Tables **4.1** and **4.2** and **Figure 4.1**. Examination of **Figure 4.1** shows bridging lithium atoms with three coordinated molecules of Et_2O, one to Li1, two to Li2. The N-Li distances are 1.995 Å Li1-N2, 2.016 Å Li1–N1, and 2.082 Å Li2-N1and 2.166 Å Li2-N2. The slightly longer Li2-N bond distances can be attributed to lower electron density contributed by the two nitrogen atoms as a result of the additional electron density contributed by the second molecule of coordinated Et_2O. Steric crowding by the PhBr group may be responsible for limiting the coordination of Et_2O to a single molecule for Li1. Although the solid-state structures of **4.5** and **4.6** have not yet been obtained, given the similarity in the NMR characterization of these species, analogous species at least in the solution state, featuring dimetallated ligand with bridging N-M-N interactions, can be anticipated.

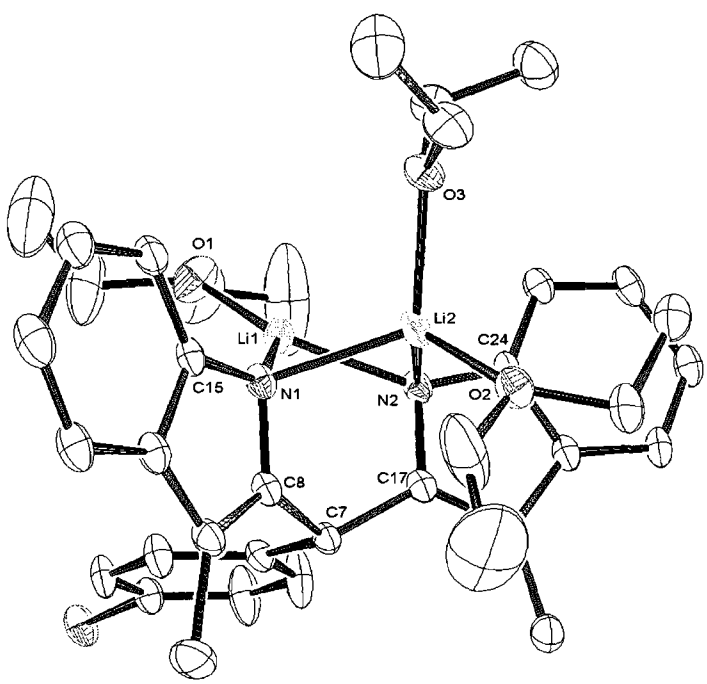


Figure 4.1: Solid-state structure of **4.4.** Thermal ellipsoids are shown at 20% probability.

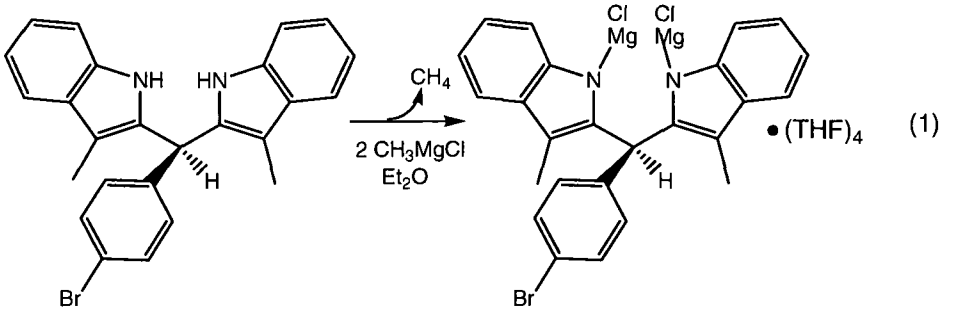
Table 4.1 Selected Bond Lengths (Å) and Angles (deg) for 4.4

A	B	Distance	A	B	C	Angle
Li1	N1	2.016(15)	N1	Li1	N2	89.9(6)
Li1	N2	1.995(13)	N1	Li1	O1	130.1(5)
Li2	N1	2.082(13)	N2	Li1	O1	140.0(7)
Li2	N2	2.166(14)	N1	Li2	N2	83.7(5)
Li1	O1	1.810(17)	N1	Li2	O2	117.6(6)
Li2	O2	2.003(17)	N2	Li2	O2	120.3(6)
Li2	O3	2.012(12)	N1	Li2	O3	112.5(6)
			N2	Li2	O3	120.3(7)
Non-Bonding Distance			O2	Li2	O3	102.6(6)
A	**B**	**Distance**	Li1	N1	C8	28.1(3)
			Li1	N1	C15	135.2(6)
Li1	Li2	2.67(2)	Li2	N1	C8	106.0(5)
			Li2	N1	C15	117.7(6)
			Li1	N2	C17	142.4(6)
			Li1	N2	C24	111.2(5)
			Li2	N2	C17	109.8(5)
			Li2	N2	C24	94.3(5)

Table 4.2 Selected Crystal Data and Collection Parameters for **4.4**

empirical formula	$C_{37}H_{49}BrLi_2N_2O_3$
formula weight	663.57
T (K)	200(2)K
λ(Å)	0.71073
crystal system	monoclinic
space group	P 2_1/c
a (Å)	14.137(6)
b (Å)	14.171(6)
c (Å)	18.698(8)
α (deg)	90
β (deg)	90
γ (deg)	100.066(6)
V (Å^3)	3688.(3)
Z	4
Abs. coeff. (mm^{-1})	1.149
Final R indices	R1 = 0.1379
	wR2 = 0.2878

The synthetic scheme for the group 1 metals can be easily extended to the addition of di(3-methylindol-2-yl)-4-bromophenylmethane to the Grignard reagent $MgCH_3Cl$. Reaction of 2 equivalents of $MgCH_3Cl$ with di(3-methylindol-2-yl)-4-bromophenylmethane in Et_2O resulted in vigourous bubbling and within 2 hours quantitative formation of **4.7** (**Scheme 4.2**). The proposed identity of **4.7** is consistent with both ^1H and ^{13}C NMR spectroscopy, which show a single product indicating that reaction of a Grignard reagent with diindolylmethane does not result in a Schlenk equilibrium in solution. However, it is impossible from this NMR data to differentiate between the proposed dimetallated product and a product featuring one magnesium atom. It is speculated that the dimetallated product is formed because there was no evidence for formation of products such as $MgCl_2$ or HCl which would likely result from a Schlenk-type redistribution of the substituents at magnesium to give a monometallated product. Nonetheless, this possibility cannot be discounted. The product **4.7** has proven reactive with Group 13 halides MX_3 (M = B, Al), although products from these reactions have yet to be isolated and characterized.

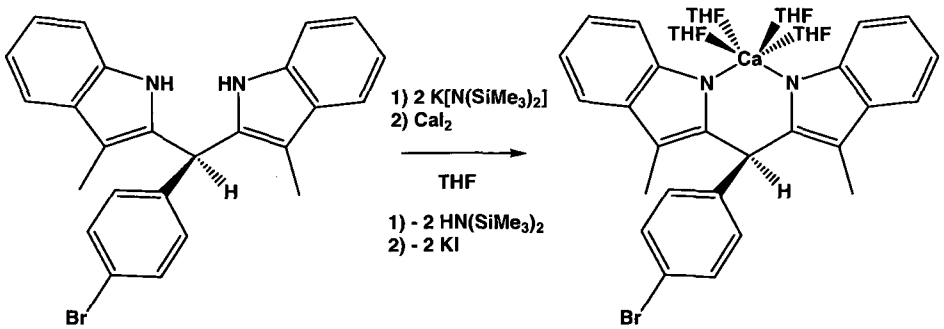


4.7

Scheme 4.2: Reaction of di(3-methylindol-2-yl)-4-bromophenylmethane with $MgCH_3Cl$ in attempt to synthesize **4.7**

IV Synthesis of Ca-di-(3-methylindolyl)-4-bromophenylmethane*$(THF)_6$

Coordination of the di(3-methylindolyl)-4-bromophenylmethane ligand to a single Group 2 s-block metal atom was the next logical step following the facile single-step syntheses of the dimetallated compounds **4.4-4.7**. Calcium was chosen due to the previously-described abundance of similar calcium complexes with successful catalytic applications. Salt metathesis reactions involving the di-metallated ligand with CaI_2 were employed, with the potassium salt **4.6** yielding the cleanest single product as analyzed by ^1H NMR. As KI has the highest lattice energy of any of the common alkali-metal halogen salts and therefore the greatest driving force for metathesis to occur, this result was not surprising. The reaction was carried out according to **Scheme 4.3**, with CaI_2 added *in situ* after deprotonation of the ligand in THF with two equivalents of $K[N(SiMe_3)_2]$. Single-crystal X-ray diffraction analysis results are summarized in **Tables 4.3** and **4.4** and **Figure 4.2**. Results indicated the product of the reaction was **4.8**, with the solid-state structure showing four directly coordinated THF molecules and two additional co-crystallized molecules of THF. The ^1H NMR spectrum showed agreement with the crystal structure as ^1H NMR signals corresponding to the protons of THF integrated for six equivalents of THF and all ligand proton resonances, save for the NH protons, were shifted from the resonances of the free ligand.



4.8

Scheme 4.3 Synthesis of Ca(THF)$_4$di(3-methylindol-2-yl)-4-bromphenylmethane **4.8** via the potassium salt

The structure shows a distorted octahedral calcium centre, with the angles E-Ca-E (E = N,O) deviating somewhat from the ideal 90°; E-Ca-E angles range from the 83.37(17)° of the N1-Ca-N2 angle to the 94.12(15)° of the N1-Ca-O2 angle. The N1-Ca-N2 angle shows the greatest deviation from 90°, thus the distortion is likely attributable to the rigidity of the chelating ligand imposing the less-than-ideal N1-Ca-N2 angle.

One of the major differences between **4.8** and the calcium β-diiminate and polypyrazolylborate complexes discussed earlier in this chapter is that the diindolylmethane ligand is dianionic, whereas the β-diiminate and polypyrazolylborate ligands are monanionic. The calcium(II) centres in the β-diiminate and polypyrazolylborate structures feature an additional monanionic ligand: a second β-diiminate ligand or a bis(trimethylsilyl)amide ligand in the cases of the β-diiminate complexes, and a 2,6-diisopropylphenoxy ligand or a bis(trimethylsilyl)amide ligand in the cases of the polypyrazolylborate structures. One might anticipate that with a second monoanionic ligand coordinating to calcium, the observed Ca-N bond lengths for both of these complexes would be significantly longer than the 2.367(5)Å for Ca-N1 and

2.356(5)Å for Ca-N2 observed for **4.8**. This is the case for the polypyrazolylborate ligands, which feature Ca-N bonds in the range of 2.412(1)Å to 2.4507(2)Å,[1e] as well as for a reported calcium di(dipyrromethene) complex, which has Ca-N bond lengths reported between 2.502(5)Å and 2.516(5)Å.[14] Interestingly, however, the bond lengths found for **4.8** fall in the middle of the range of Ca-N bond lengths reported for calcium β-diiminate complexes, which vary between 2.313(1)Å and 2.384(1)Å.[1e,9,10] Although the β-diiminate and di(3-methylindol-2-yl)-4-bromophenylmethane ligands are much different structurally, the sterics specifically about the calcium centre are not dissimilar, indicating that a comparison of bond lengths may be essentially a comparison of electronics. Thus, the amount of electron density donated by the nitrogen atoms of the formally -1 β-diiminate ligand and the amount donated by the nitrogen atoms of the formally -2 diindolylmethane ligand may well be similar.

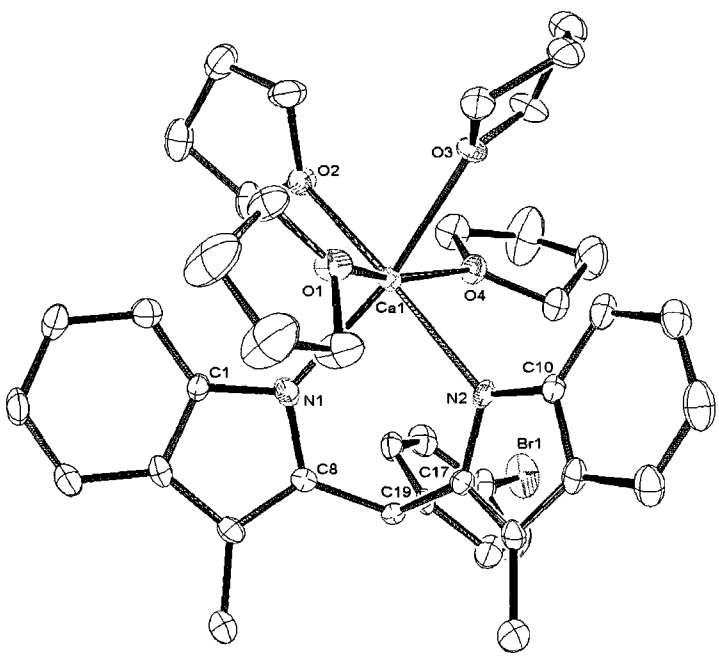


Figure 4.2: Solid-state structure of **4.8.** Thermal ellipsoids are shown at 50% probability.

Table 4.3 Selected Bond Lengths (Å) and Angles (deg) for 4.8

A	B	Distance	A	B	C	Angle
Ca	N1	2.367(5)	Ca	N1	N2	82.37(17)
Ca	N2	2.356(5)	Ca	N1	C1	126.8(4)
Ca	O1	2.422(4)	Ca	N1	C8	126.2(4)
Ca	O2	2.405(4)	Ca	N2	C10	123.9(4)
Ca	O3	2.413(4)	Ca	N2	C17	126.4(3)
Ca	O4	2.417(4)	Ca	N1	O1	82.49(16)
			Ca	N1	O2	94.12(15)
			Ca	N1	O3	164.54(16)
Contacts			Ca	N1	O4	113.31(15)
			Ca	N2	O1	90.04(16)
Ca	O5	6.008	Ca	N2	O2	167.41(15)
Ca	O6	9.923	Ca	N2	O3	103.52(15)
			Ca	N2	O4	86.95(15)
			Ca	O1	O2	101.52(14)
			Ca	O1	O3	83.21(14)
			Ca	O1	O4	163.30(14)
			Ca	O2	O3	82.99(13)
			Ca	O2	O4	83.34(14)
			Ca	O3	O4	81.54(14)

Table 4.4 Selected Crystal Data and Collection Parameters for **4.8**

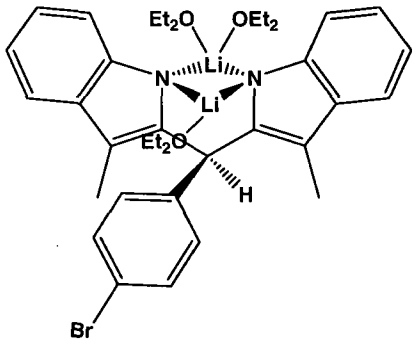
empirical formula	$C_{46}H_{61}BrCaN_2O_5$
formula weight	845.96
T (K)	203(2)K
λ(Å)	0.71073
crystal system	monoclinic
space group	$P\ 2_1/n$
a (Å)	13.368(2)
b (Å)	12.682(2)
c (Å)	27.981(5)
α (deg)	90
β (deg)	96.074(3)
γ (deg)	90
V (Å^3)	4716.8(14)
Z	4
Abs. coeff. (mm^{-1})	1.023
Final R indices	R1 = 0.0780
	wR2 = 0.1937

Experimental Section

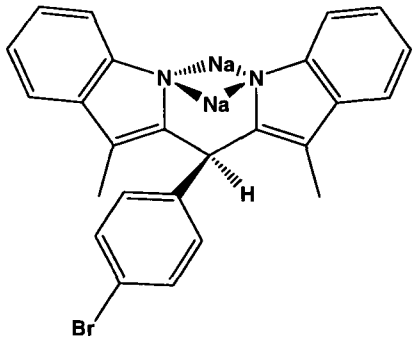
General Considerations All manipulations were carried out under nitrogen employing standard drybox techniques. All solvents were sparged with nitrogen and dried by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Deuterated chloroform and dichloromethane were dried by addition of molecular sieves. Di-(3-methylindol-2-yl)-4-bromophenylmethane was prepared according to a previously reported procedure.[15] All other reagents were purchased from Aldrich and used as received. NMR spectra were run on Bruker Avance 300 and 500 MHz spectrometers with deuterated benzene as the solvent using residual protons of the deuterated solvent for reference. Elemental analysis was performed by Midwest Microlabs, Indianapolis, Indiana.

*Dilithio-di-(3-methylindol-2-yl)-4-bromophenylmethane*3 Et_2O* **4.4** 0.29mL (4.7mmol) n-butyllithium (1.6M solution in n-hexanes) was added dropwise to a room-temperature suspension of 0.100g (0.233mmoles) di-(3-methylindolyl)-4-bromophenylmethane in diethyl ether. Immediate bubbling ensued with concomitant colour change to golden yellow and then within minutes to purple. After 2 hours, solvent was removed *in vacuo*. Dark purple solid was washed with hexanes and recrystallized from THF at -22 C°. Yield: quantitative ^{1}H NMR(CD_2Cl_2): 1.67 [m, 16H, $O(CH_2)_2(CH_2)_2$, $^3J_{HH}$ = 6.6 Hz], 2.46 (s, 6H, 2 CH_3), 3.31 [m, 16H, $O(CH_2)_2(CH_2)_2$, $^3J_{HH}$ = 6.4 Hz], 5.87 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 6.64 (d, 2H, *H*Ar, $^3J_{HH}$ = 8.0 Hz) 6.85 (m, 4H, *H*Ar, $^3J_{HH}$ = 6.2 Hz), 7.20 (d, 2H, *H*Ar, $^3J_{HH}$ = 8.5 Hz), 7.25 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.6 Hz), 7.45 (m, 2H, *H*Ar, $^3J_{HH}$ = 7.0 Hz) ^{13}C NMR (C_6D_6): 9.69 (*C*Me), 25.80 [$O(CH_2)_2(CH_2)_2$], 40.66 (*C*H(3-

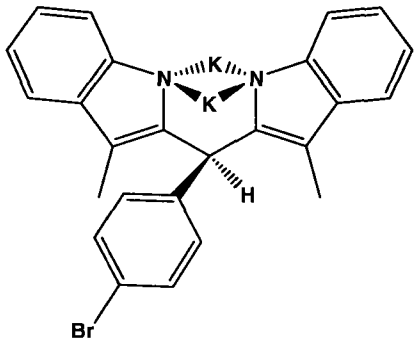
methylindolyl)$_2$), 68.55 [O(CH_2)$_2$(CH_2)$_2$], 107.30 (*C*Ar), 115.13 (*C*Ar), 115.99 (*C*Ar), 117.66 (*C*Ar), 117.98 (*C*Ar), 119.83 (*C*Ar), 130.35 (*C*Ar), 131.54 (*C*Ar), 132.93 (*C*Ar), 146.89 (*C*Ar), 147.51 (*C*Ar), 147.69 (*C*Ar) Anal. Calcd. For $C_{33}H_{39}BrLi_2N_2O_2$ (2 coordinating Et_2O): C 67.24, H 6.67, N 4.75 Anal. Calcd. For $C_{31}H_{34}BrLi_2N_2O_{1.5}$ (1.5 coordinating Et_2O): C 67.40, H 6.20, N 5.07 Found: C 65.20, H 6.13, N 4.83



*Disodium-di-(3-methylindol-2-yl)-4-bromophenylmethane*4THF* **4.5** To a clear, colourless solution of 0.110g (0.256 mmol) di-(3-methylindolyl)-4-bromophenylmethane in 2 mL THF was added 0.020g (0.51 mmol) sodium amide. Solution immediately turned pale yellow, becoming deeper yellow within minutes. Slight bubbling was observed. After 3 hours stirring, THF was removed *in vacuo* and yellow solid was washed with hexanes (2 x 1mL) to yield 0.193 g yellow solid. **Yield:** 99% ^{1}H NMR (CD_2Cl_2): 1.68 (m, 16H, 4 x CH_2 of THF), 2.43 (s, 6H, 2x CH_3), 3.35 (m, 16H, 4 x CH_2 of THF), 5.85 (s, 1H, CH), 6.62 (d, 2H, *H*Ar) , 6.85 (m, 4H, *H*Ar), 7.21 (m, 4H, *H*Ar), 7.43 (d, 2H, *H*Ar)

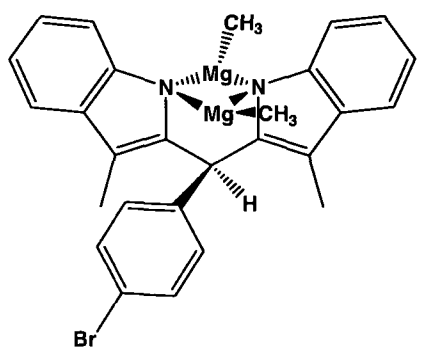


*Dipotassium-di-(3-methylindolyl)-4-bromophenylmethane*4THF* **4.6** To a clear, colourless solution of 0.073g (0.170 mmol) di-(3-methylindolyl)-4-bromophenylmethane in 2 mL THF was added 0.068g (0.34 mmol) potassium bis(trimethylsilyl)amide. Solution immediately turned dark yellow, then within minutes became red, then purple. After 3 hours stirring, THF was removed *in vacuo* and remaining purple solid was washed with hexanes (2 x 1mL) to 0.119g yield yellow solid. **Yield** (if 4 co-ordinated THF): 88.2% ^{1}H NMR: insoluble in common NMR solvents



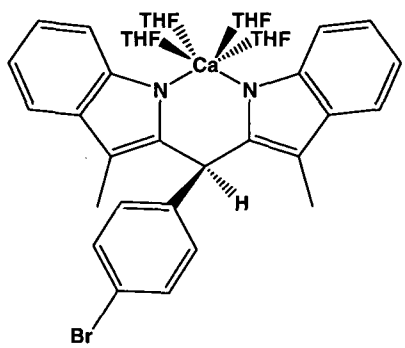
Attempted Synthesis of di-(3-methylindol-2-yl)(dichloromagnesium)-4-bromophenylmethane **4.7** 0.29mL (0.46mmol) methylmagnesiumchloride (1.6M solution in diethyl ether) was added dropwise to a room-temperature suspension of 0.100g (0.233 mmol) di-(3-methylindolyl) -4-bromophenylmethane in diethyl ether or THF. Immediate

bubbling ensued as the white suspension became a clear, colourless solution within 5 minutes. Within 30 minutes, the mixture had reverted to a white suspension. The precipitate was isolated by suction filtration, washed with diethyl ether (3 x1.5mL) and dried *in vacuo* to yield 0.114 g white solid. **Yield** (if dimetallated product)**:** 89.6% ^{1}H NMR($CDCl_3$): 1.67 [m, 16H, $O(CH_2)_2(CH_2)_2$, $^{3}J_{HH}$ = 6.6 Hz], 2.48 (s, 6H, 2 CH_3), 3.31 [m, 16H, $O(CH_2)_2(CH_2)_2$, $^{3}J_{HH}$ = 6.0 Hz], 5.95 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 6.63 (d, 2H, *H*Ar, $^{3}J_{HH}$ = 8.4 Hz) 6.95 (m, 4H, *H*Ar, $^{3}J_{HH}$ = 7.0 Hz), 7.02 (m, 2H, *H*Ar, $^{3}J_{HH}$ = 7.4 Hz), 7.12 (d, 2H, *H*Ar, $^{3}J_{HH}$ = 8.5 Hz), 7.57 (m, 2H, *H*Ar, $^{3}J_{HH}$ = 7.4 Hz) ^{13}C NMR (C_6D_6): 9.25 (*C*Me), 14.10 [$O(CH_2)_2(CH_2)_2$], 39.86 (*C*H(3-methylindolyl)$_2$), 66.79 [$O(CH_2)_2(CH_2)_2$], 107.96 (*C*Ar), 112.42 (*C*Ar), 115.89 (*C*Ar), 117.92 (*C*Ar), 118.14 (*C*Ar), 119.00 (*C*Ar), 121.88 (*C*Ar), 130.33 (*C*Ar), 130.58 (*C*Ar), 131.56 (*C*Ar), 144.51 (*C*Ar), 145.82 (*C*Ar)



*Calcium di-(3-methylindol-2-yl)-4-bromophenylmethane*6THF* **4.8** To a clear, colourless solution of 0.103g (0.240 mmol) di-(3-methylindolyl)-4-bromophenylmethane in 2 mL THF was added 0.096g (0.48 mmol) potassium bis(trimethylsilyl)amide. Solution immediately turned dark yellow, then within minutes turned to red, then purple. After 3 hours stirring, 0.070 g (0.24 mmol) CaI_2 (white, crystalline, light-sensitive solid) was added to the reaction mixture. Reaction vessel was then wrapped in black tape to block

light and allowed to stir. After 24 hours, reaction mixture was now a white slurry. When allowed to settle, a white precipitate separated from the yellow solution. This precipitate was removed by suction filtration. To the yellow filtrate was added 2 mL hexanes which immediately resulted in formation of a second white precipitate. This was isolated by suction filtration, redissolved in a minimum amount of THF and crystallized by slow diffusion of hexanes into the saturated THF solution at -22°C. **Yield:** 0.096g, 53% NMR(CD_2Cl_2): 1.80 [broad s, 24H, $O(CH_2)_2(CH_2)_2$], 2.45 (s, 6H, 2 CH_3), 3.63 [broad s, 24H, $O(CH_2)_2(CH_2)_2$], 6.08 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 6.78 (m, 4H, *H*Ar, $^3J_{HH}$ = 6.5 Hz) 6.97 (s, 2H, *H*Ar), 7.04 (d, 2H, *H*Ar, $^3J_{HH}$ = 8.0 Hz), 7.27 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.6 Hz), 7.40 (m, 2H, *H*Ar, $^3J_{HH}$ = 6.9 Hz) ^{13}C NMR (CD_2Cl_2): 9.76 (*C*Me), 26.06 [$O(CH_2)_2(CH_2)_2$], 41.79 (*C*H(3-methylindolyl)$_2$), 68.65 [$O(CH_2)_2(CH_2)_2$], 105.82 (*C*Ar), 111.34 (*C*Ar), 113.37 (*C*Ar), 115.17 (*C*Ar), 117.68 (*C*Ar), 118.98 (*C*Ar), 119.94 (*C*Ar), 122.26 (*C*Ar), 131.37 (*C*Ar), 131.66 (*C*Ar), 145.80 (*C*Ar), 148.19 (*C*Ar)



Structural determination of 4.8

A single crystal was mounted on a thin glass fibre and held using viscous oil. It was subsequently cooled to the collection temperature. Crystal data and measurement details are summarized in **Tables 2.1** and **2.2**. Data was collected on a Bruker AX SMART 1k CCD diffractometer using 0.3o ω-scans at 0, 90 and 180 in ϕ. Unit-cell parameters were obtained from 60 frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied (Blessing, R. *Acta Cryst.* **1995**, *A51*, 33-38). Direct methods were used to solve molecular structures and connectivity, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.1 program library (Sheldrick, G.M., Bruker AXS, Madison, WI, 1997).

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Chapter 5

Phosphorus and Antimony Compounds of Diindolylmethane: Synthesis and Characterization

I Introduction

II Synthesis of Diindolylmethane Phosphine Halides

III Attempted Halide Abstractions to Yield Phosphenium Cations

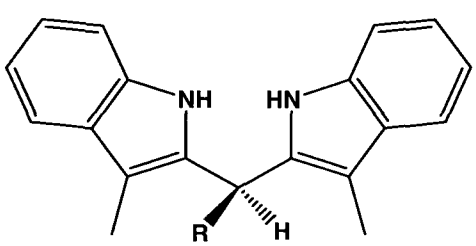
IV Synthesis of a Di(3-methylindol-2-yl)-4-bromophenylmethane Stibine

V Attempted Conversion to a Stibenium Ion via a Protonation Route

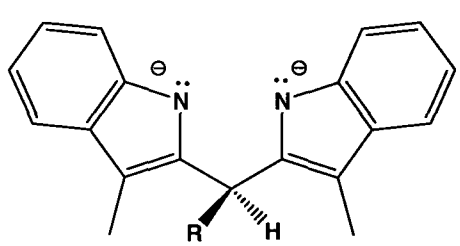
Phosphorus and Antimony Compounds of Diindolylmethane: Synthesis and Characterization

I Introduction

The diindolylmethane scaffold **5.1** can be deprotonated and employed as a dianionic diamido ligand **5.2** and the steric and electronic properties of this dianion are fundamentally different from other amido ligands.[1] The coordination chemistry of **5.2** is relatively underexplored. Although there are a few reported examples of triindolylmethane phosphine complexes,[2] to the best of our knowledge no diindolylmethane complexes of Group 15 elements are reported in the literature. The steric bulk of the ligand and relatively low π-donating ability of the indole nitrogen atoms imparts potential to synthesize π-acidic Group 15 complexes and to probe their Lewis acid/base properties. Furthermore, such species could be used to investigate several avenues of utility as synthetic reagents, including potentially providing a route to access Group 15 cations or new metal complexes. Herein we present the synthesis and characterization of diindolylmethane halophosphines and a diindolylmethane aminostibine, the first examples of Group 15 diindolylmethane complexes.



5.1



5.2

II Synthesis of Diindolylmethane Phosphine Halides

Mono-halogenated phosphines, particularly those ligated by chelating amido ligands to form N-heterocycles, are a synthetically useful category of compound due in large part to the control afforded by restricting probable reactivity to removal or substitution of the halogen atom.[3] N-heterocyclic phosphenium (NHP) cations derived from these compounds are used in diverse types of inorganic chemistry, including reversible cycloaddition chemistry, azide and phosphazene chemistry, hydride and small-molecule activation chemistry, synthesis of reactive, polarized diphosphine complexes, and most commonly syntheses of transition metal catalysts featuring NHP ligands.[3] Uses of phosphenium ions as synthons will be discussed further in the next section.

Neutral phosphines featuring relatively inert R-groups as substituents represent the majority of phosphines which are used as ligands. However, several examples of monohalogenated N-heterocyclic phosphines ligating to metals are reported, where reactivity of the halogen atom is induced after coordination to a metal[4] indicating that the more reactive halophosphines are applicable as ligands as well. Substitution of the halogen atom of an N-heterocyclic halophosphine is also a route to high molecular-weight phosphazene polymers featuring repeating N-heterocyclic phosphine units.[5]

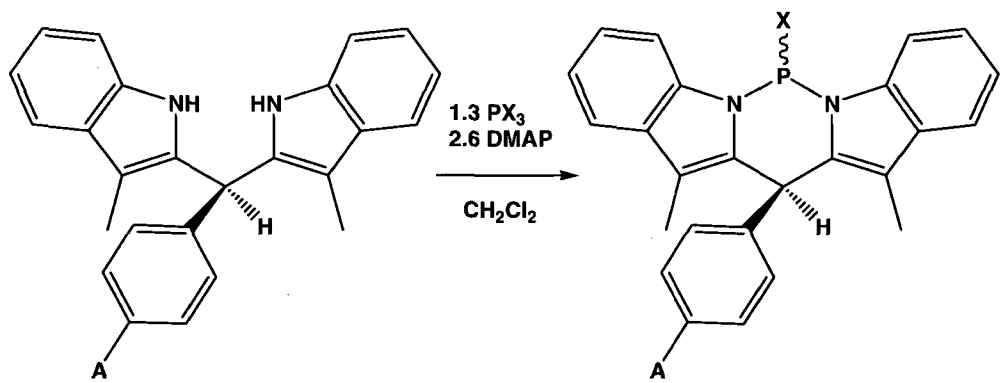
Dehydrohalide coupling reactions are a convenient means commonly used to bind a ligand to a non-metallic main group element. Dehydrohalide coupling involves a ligand reacting with an element-halide compound, EX_n, which results in concomitant removal of proton(s) from the ligand and loss of the halogen atom(s) from EX_n, forming a new ligand-element bond and producing the haloacid HX as a by-product. To ensure that the HX by-product does not react with the new product to give the reverse reaction or other

unwanted reactions, a base "scavenger" is usually present in the reaction mixture to neutralize HX.

In contrast, salt metathesis reactions are commonly used to bind ligands to metal halides MX_n, as the metal salt by-products formed by metathesis tend to precipitate from the reaction mixture, driving the reaction to completion by Le Chatelier's principle. Le Chatelier's principle does not generally apply for dehydrohalide coupling reactions as the acid by-products HX remain in solution. However, as salt metathesis reactions tend to work less well with "softer," non-metallic main group halides, the dehydrohalide coupling approach is used most often to ligate these compounds.

Therefore, dehydrohalide coupling methods were used to generate the halophosphine products **5.3**. Addition of 1.3 equivalents of PX_3 (X = Cl, Br) to the di(3-methylindol-2-yl)-4-bromophenylmethane ligand in CH_2Cl_2, immediately followed by addition of 2.6 equivalents of DMAP followed by stirring for 3 days, after removal of volatiles and extraction with THF yielded the products in moderate yield. Detailed structural features for **5.3a** were established using single-crystal x-ray diffraction analysis on crystals grown by slow diffusion of hexane vapours into a saturated CH_2Cl_2 solution of **5.3a**. These results are summarized by the structure shown in **Figure 5.1** and the data presented in **Tables 5.1** and **5.2**. The compounds **5.3a-c** were characterized by ^{1}H, ^{31}P and ^{13}C NMR spectroscopy. All NMR spectra appear to show a mixture of products in ~3:1 ratio, which was initially attributed to some formation of a di(dihalophosphine) product resulting from the excess of PX_3 /DMAP used. However, when the reaction was undertaken using the ligand:PX_3:DMAP in an exact 1:1:2 ratio, the minor product persisted in approximately the same ratio as evidenced by NMR despite our best efforts

to isolate a single substance by extraction or recrystallization methods. This has lead us to believe that the mixture of NMR-distinct products is the result of formation of two separate stereoisomers of **5.3a-c**: one in which the halide atom X juts perpendicular to the plane of the N-P-N heterocycle in the same direction as the aryl moiety (as shown in the solid-state structure in **Figure 5.1**), and one in which the lone pair of phosphorus is on the same side of the plane of the N-P-N heterocycle as the aryl moiety, with the halide atom pointing opposite. It is speculated that the isomers with the halide atom on the same side of the plane of the heterocycle as the aryl group are the major products since probability dictates that a crystal would be isolated from the major product.



5.3

5.3a: X = Cl, A = Br
5.3b: X = Br, A = Br
5.3c: X = Cl, A = F

Scheme 5.1: Synthesis of Di(3-methylindol-2-yl)phenylphosphines **5.3a-c** (X = Cl, Br; A = Br,F)

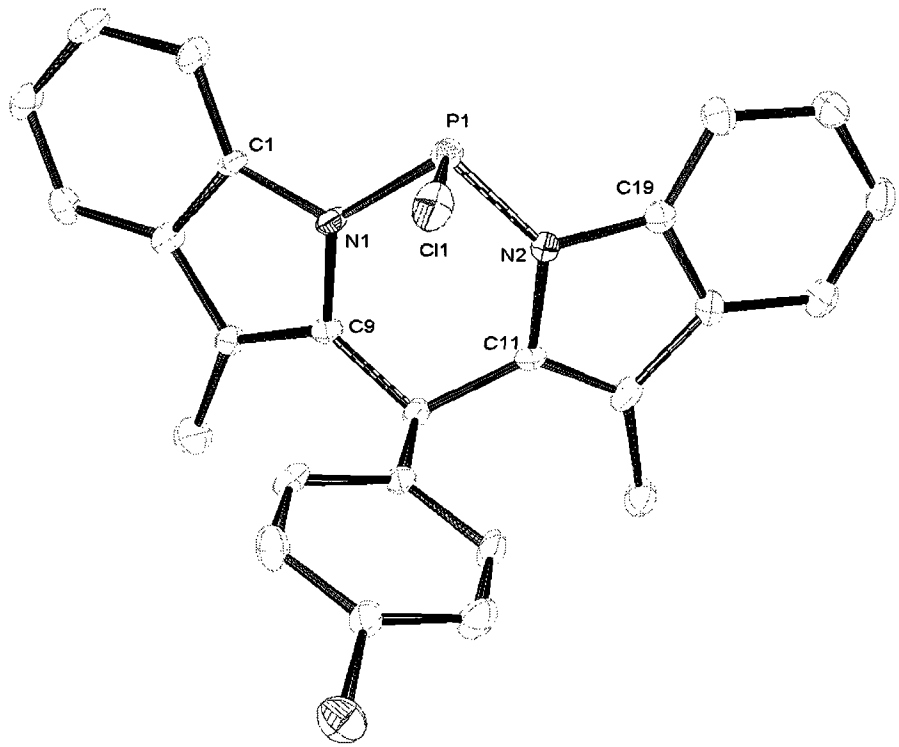


Figure 5.1: Solid-State structure and numbering scheme of **5.3a**. One co-crystallized molecule of toluene has been omitted. Thermal ellipsoids are drawn at 20% probability.

Table 5.1 Selected Bond Lengths (Å) and Angles (deg) for 5.3a

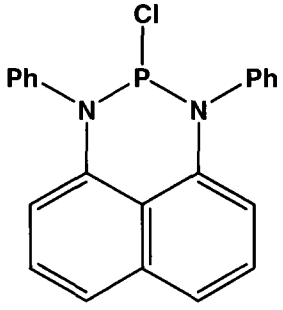
A	B	Distance	A	B	C	Angle
P	Cl	2.108(3)	Cl	P	N1	101.5(2)
P	N1	1.689(6)	Cl	P	N2	101.0(2)
P	N2	1.676(6)	N1	P	N2	96.8(3)
			P	N1	C1	122.9(5)
			P	N2	C19	123.5(5)
			P	N1	C9	128.3(5)
			P	N2	C11	129.5(5)

Table 5.2 Selected Crystal Data and Collection Parameters for **5.3a**

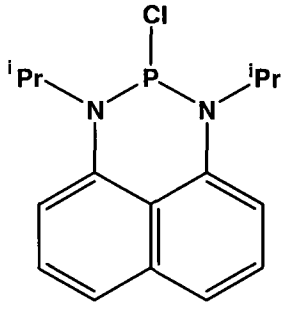
empirical formula	C_{32} H_{27} N_2 P Cl Br
formula weight	585.89
T (K)	213(2)K
λ(Å)	0.71073
crystal system	orthorhombic
space group	Pbca
a (Å)	10.836(4)
b (Å)	21.630(8)
c (Å)	23.468(8)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	5501(3)
Z	8
Abs. coeff. (mm^{-1})	1.674
Final R indices	R1 = 0.0560
	wR2 = 0.1224

A degree of ambiguity in the information gained by obtaining the solid-state structure of **5.3a** makes it difficult to infer comparative Lewis acid-base properties of diindolylmethane. The N-heterocyclic chlorophosphines **5.4**,[6] **5.5**,[6] and **5.6**[7] have been chosen for purposes of comparison as they are among the compounds most similar to **5.3a** for which there is structural data available in the literature. Comparing relative P-N bond lengths should be an indication of the amount of electron density donated by the nitrogen atoms of each ligand, with the diindolylmethane ligand expected to have longer P-N bonds due to less π-donation from the lone pair on nitrogen. This lone pair is participating in the indole aromatic system, whereas the lone pairs for the ligands of **5.4**, **5.5**, **5.6** are not. The P-N bond lengths of 1.689(6)Å and 1.676(6)Å for **5.3a** are slightly longer than the P-N bond lengths of 1.670(2)Å for both P-N bonds in **5.5**[6] and the bond lengths of 1.6684(13)Å and 1.6678(13)Å for **5.6**,[7] but their average is inside the margin of error for the P-N bond lengths of 1.678(2)Å and 1.681(2)Å found for **5.4**,[6] which

makes it difficult to infer definitively whether the aromaticity of the nitrogen atoms in **5.3a** hinders their Lewis donation abilities as expected. However, the P-Cl bond length of 2.108(2)Å in **5.3a** is slightly shorter than the P-Cl bond lengths of 2.148(1) Å of **5.4**,[6] 2.1723(9) Å of **5.5**,[6] and 2.1993(6) Å of **5.6**,[7] indicating that perhaps additional electron density in the N-P-N system of **5.3a** comes from the chlorine atom. The chlorine atom can then be viewed as compensating for less electron density donated by the nitrogen atoms, which supports the hypothesis that the nitrogen atoms of diindolylmethane are poorer donors than in **5.4**, **5.5**, and **5.6**, but calls into question the hypothesis that this would therefore make the phosphorus centre more Lewis acidic.



5.4



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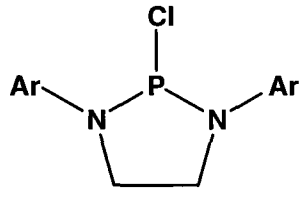


Ar = *p*MeOPh

5.6

III Attempted Halide Abstractions to Yield Phosphenium Cations

N-heterocyclic phosphenium ions (NHP's) are di-coordinate species with a single lone pair and a total of six valence electrons – analogues of carbenes, though their existence in fact pre-dates that of isolated N-heterocylic carbenes (NHC's).[8,9] Prior to the advent of NHC ligands, phosphine ligands were the most prevalent on catalytic metal complexes; however, the increased prevalence of carbene ligands also brought increased examination of the isoelectronic phosphenium ions for use as ligands, not in the least because, despite their isovalency, their electronic properties are quite distinct.[10,11,12]

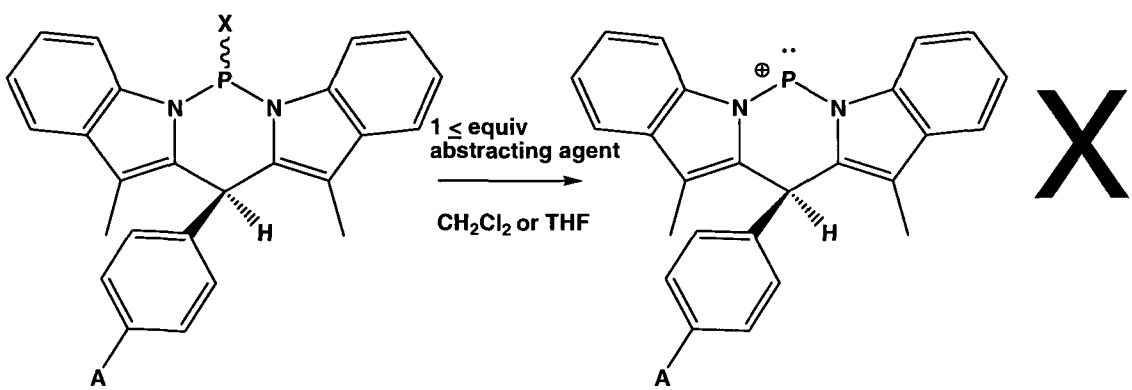
While NHC's are considered nucleophilic, phosphenium ions are classified as electrophilic and this difference allows for variation of the electronics at a metal centre by varying from a NHC ligand to a phosphenium ligand. Like their NHC analogues, phosphenium ions are commonly stabilized within N-heterocycles by the π-donating effect of two adjacent nitrogen atoms.

Further uses for NHP ions are found in main group chemistry. NHP ions stabilized by dative interaction with another phosphine – which also can be viewed as unsymmetrical diphosphanes, if the P-P interaction is represented covalently – are one area of research where phosphenium ion chemistry is redefining fundamental structure and bonding paradigms.[13] NHP ions have also been of synthetic importance as the "by-product" in reactions where phosphines are used as hydride sources to perform simple reductions of small carbonyls in a similar manner to the more common metal hydride reagents such as $LiAlH_4$.[14,15] These are just two examples of how NHP ions have become increasingly versatile synthetic tools.

The adjacent nitrogen atoms of a proposed diindolylmethane NHP would be poorer π-donors than nitrogen atoms in common non-aromatic NHP ions. It was therefore postulated that a diindolylmethane NHP ion would feature a particularly electrophilic phosphorus centre, though its lesser amount of stabilizing π-density could make it more difficult to achieve. A common method to synthesize NHP ions suitable to our purposes is from N-heterocylic phosphine halides by abstraction of the halide.

Repeated attempts to abstract the halide from compounds **5.3a-c** to generate a phosphenium ion using halide abstraction agents AgOTf, TMSOTf, $GaCl_3$ and $B(C_6F_5)_3$ according to **Scheme 5.2** were unsuccessful, resulting in a mixture of products by NMR,

none of which displayed resonances in the ^{31}P NMR spectrum near the 150-250 ppm range expected for NHP ions.[3,16] Despite following identical procedures to literature NHP ion syntheses, a major product could not be isolated or identified. Variation of solvent from CH_2Cl_2 to THF, adding large excesses of the abstracting reagents, and attempts to isolate single products by crystallization were unsuccessful. The three different di(3-methylindol-2-yl)phenylmethane phosphine halide compounds **5.3a-c** were synthesized to vary the electronics of the phosphorus atom by varying the halogen bonded to the phosphorus centre (X= Cl, Br) and the halogen at the para-position of the phenyl group of the ligand (Y= Br, F; F was postulated to be much less likely to react with the species intended to abstract halogen atoms from phosphorus). None of the varieties of phosphine complex reacted with any abstracting agent to give results which either showed a single major product by ^{1}H or ^{31}P NMR or a ^{31}P resonance in the expected NHP region.



Scheme 5.2: Attempted Synthesis of NHP ions

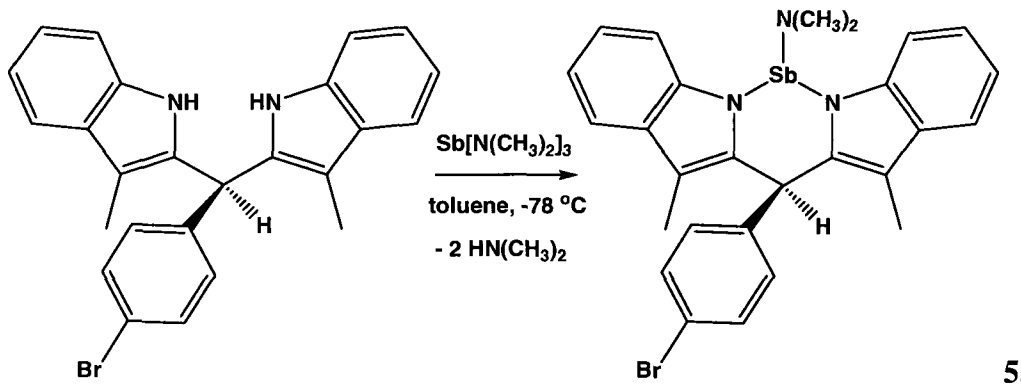
IV Synthesis of a Di(3-methylindol-2-yl)-4-bromophenylmethane Stibine

Group 15 elements below phosphorus are far less commonly used in ligands than phosphorus itself. Nonetheless, there are some examples of arsenic and antimony compounds used in catalysis and other applications. Dimethylstibino esters have proven active catalysts in the living radical polymerization of conjugated and unconjugated vinyl monomers.[17] Antimony has also been ligated by bulky organic ligands for the creation of more stable and easier to manipulate reagents,[18,19] and ligands have been coordinated to transition metals through antimony donors.[19] Among amido chemistry of antimony, tris(amido)stibine complexes have been synthesized for use as ligands,[20] while the chemistry of bis(amido)diazastibines has been explored as part of a series of investigations of heterocyclic chemistry of the heavier Group 15 elements.[21] Therefore, because there was precedent for useful organostibine and amidostibine compounds it was decided to investigate reactivity with antimony reagents in attempts to synthesize diindolylmethane stibines. As well, there was fundamental interest in investigating the chemistry of the diindolylmethane ligand framework with heavier main group elements, whose greater atomic radii and poorer orbital overlap with the orbitals of the nitrogen donors could potentially influence the chemistry to be significantly different from the chemistry of diindolylmethane phosphines.

A diindolylmethanehalostibine proved unattainable using dehydrohalide coupling methods with SbI_3, possibly because SbI_3 exists as a tetramer where the iodine atoms bridge the Sb centre, whereas the halophosphines successfully employed using this methodology are monomeric molecules. Thus, methodology analogous to that used to generate an amidostibine of diaminonaphthalene[22] was chosen, involving transamination

of $Sb[N(CH_3)_3]$ with di(3-methylindol-2-yl)-4-bromophenylmethane at -78°C in toluene, followed by gradual warming to room temperature. Removal of volatiles resulted in formation of the diindolylmethane amidostibine **5.7** in high yield within 6 hours as a white powder. ^1H and ^{13}C NMR spectra showed the expected resonances for the ligand and the dimethylamido substituent, with the dimethylamido resonances very close to those reported for the diamidonaphthalene amidostibine.[22] Further confirmation that the product formed was indeed **5.7** was obtained by elemental analysis.

Attempts to obtain crystals of **5.7** suitable for x-ray diffraction have thus far been unsuccessful, making structural information impossible to obtain. However, the demonstration of this facile synthesis provides the first definitive evidence that diindolylmethane ligands can effectively support heavier main-group elements to form stable compounds in high yields. Prior to our work, the heaviest reported atom to which diindolylmethane had been coordinated was zirconium, and the heaviest main group atom was silicon. As reported in the previous chapter, a calcium compound has also been confirmed and the antimony compound **5.7** represents a significant step beyond that. In addition, this synthesis demonstrates that the methodology of transamination can be extended to include syntheses of diindolylmethane compounds of main group elements, adding another reaction to the hydrogen elimination, salt metathesis, and dehydrohalide coupling strategies employed to generate previous compounds in this report.



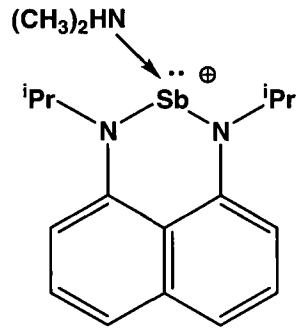
5.7

Scheme 5.3: Synthesis of di-(3-methylindol-2-yl)dimethylamidoantimony-4-bromophenylmethane **5.7**

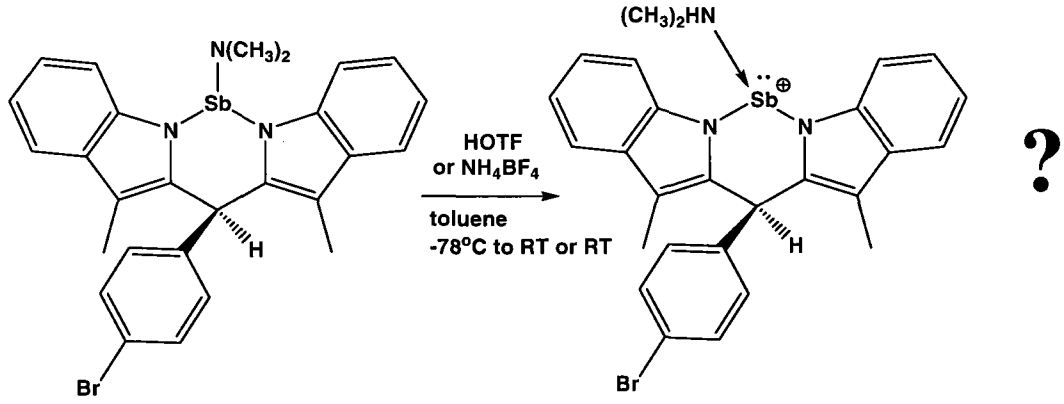
V Attempted Conversion to a Stibenium Ion via a Protonation Route

The successful synthesis of a formal stibenium cation **5.8** supported by the diamidonaphthalene framework, via protonation of the dimethylamido substituent[22] led to the idea to extend this method to the analogous diindolylmethane dimethylamidostibine **5.7**. Because **5.7**, like **5.8**, is an air- and moisture-sensitive compound, a non-aqueous Bronsted acid must be used. Triflic acid (HOTf) was used in the synthesis of **5.8**. However, when the same reaction was carried out with **5.7**, adding one equivalent of HOTf using exactly anaologous procedures, the result was formation of several products based on the ^{1}H NMR spectrum, including significant amounts of the re-protonated ligand. Using NH_4BF_4 as the acid achieved similar results based on ^{1}H NMR analysis. The reactions were both carried out at room temperature and starting at -78°C, as in the synthesis of **5.8**. These initial investigations are not extensive enough to say that a stibenium ion cannot be formed by similar methods; however, it is possible that because the nitrogen atoms of diindolylmethane are poorer donors than those of

diamidonaphthalene, a stable stibenium cation supported by the diindolylmethane framework may be more difficult to achieve.



5.8



5.8

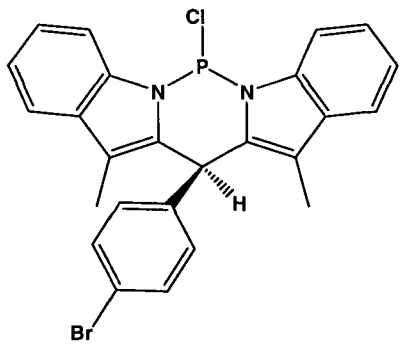
Scheme 5.4: Attempted protonation of methylamido nitrogen to give formal stibenium Cation **5.8**

Experimental

General Considerations All manipulations were carried out under nitrogen employing standard drybox or Schlenk line techniques. Dichloromethane was distilled over CaH_2 prior to use. All other solvents were sparged with nitrogen and dried by passage through a column of activated alumina using an apparatus purchased from Anhydrous Engineering. Deuterated benzene, chloroform and dichloromethane were dried by addition of molecular sieves. Di-(3-methylindol-2-yl)-4-bromophenylmethane was prepared according to a previously reported procedure.[23] Di-(3-methylindol-2-yl)-4-fluorophenylmethane was prepared according to the procedure reported in Chapter 2 of this report. Tris(dimethylamido)antimony was purchased from Strem Chemicals and used as received. All other reagents were purchased from Aldrich and used as received. NMR spectra were run on Bruker Avance 300 and 500 MHz spectrometers with deuterated benzene, chloroform or dichloromethane as the solvent using residual protons of the deuterated solvent for reference. Elemental analysis was performed by Midwest Microlabs, Indianapolis, Indiana.

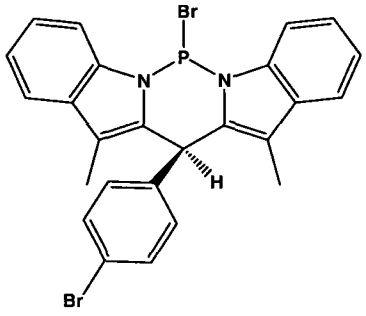
di-(3-methylindol-2-yl)chlorophosphine-4-bromophenylmethane **5.3a** PCl_3(0.050 mL, 0.57 mmol) was added dropwise to a solution of di-(3-methylindolyl)-4-chlorophenylmethane (0.189g, 0.440 mmol in 2 mL dichloromethane), followed immediately by addition of 0.140 g (1.15 mmol) DMAP. The resulting clear, yellow solution was allowed to stir for 72 hours before removal of the solvent *in vacuo*. The product was extracted with THF (3 x 1.5 mL), filtered through a glass frit and the solvent was removed *in vacuo*. The resultant off-white solid was washed with n-hexanes (3 x

1.5mL) and diethyl ether (3 x 1.5mL) and the resulting white solid was recrystallized from dichloromethane at -22 C°. **Yield:** 0.119g (54.8%) $^{31}P\{^{1}H\}$ NMR (C_6D_6, major isomer): δ = 90.3 ppm ^{1}H NMR(C_6D_6, major isomer): 2.11 (s, 6H, 2 C*H*$_3$), 5.60 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 7.16 (d, 2H, *H*Ar, $^{3}J_{HH}$ = 8.1 Hz) 7.22 (t, 2H, *H*Ar, $^{3}J_{HH}$ = 8.1 Hz), 7.25 (m, 4H, *H*Ar, $^{3}J_{HH}$ = 8.4 Hz), 7.53 (d, 2H, *H*Ar, $^{3}J_{HH}$ = 7.8 Hz), 7.65 (m, 2H, *H*Ar, $^{3}J_{HH}$ = 7.8 Hz)

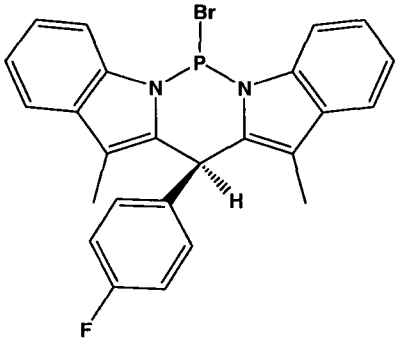


di-(3-methylindol-2-yl)bromophosphine-4-bromophenylmethane **5.3b** PBr_3 (0.050 mL, 0.53 mmol) was added dropwise to a solution of di-(3-methylindolyl)-4-bromophenylmethane (0.176g, 0.410 mmol in 2 mL dichloromethane), followed immediately by addition of 0.130 g (1.06 mmol) DMAP. The resulting dark purple solution changed to a lighter purple as the reaction proceeded. The solution was then allowed to stir for 72 hours before removal of the solvent *in vacuo*. The product was extracted with THF (3 x 1.5 mL), filtered through a glass frit and the solvent was removed *in vacuo*. The resulting dull purple solid was washed with n-hexanes (3 x 1.5mL) and diethyl ether (3 x 1.5mL) to yield product. **Yield:** 0.128g (58.0%) $^{31}P\{^{1}H\}$ NMR($CDCl_3$, major isomer): δ = 89.5 ppm (isomer 1) ^{1}H NMR($CDCl_3$, major isomer) : 2.40 (s, 6H, 2 C*H*$_3$), 5.85 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 7.08 (d, 2H,

*H*Ar, $^3J_{HH}$ = 8.4 Hz) 7.31 (m, 6H, *H*Ar, $^3J_{HH}$ = 7.6 Hz), 7.59 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.2 Hz), 7.65 (d, 2H, *H*Ar, $^3J_{HH}$ = 7.8 Hz)

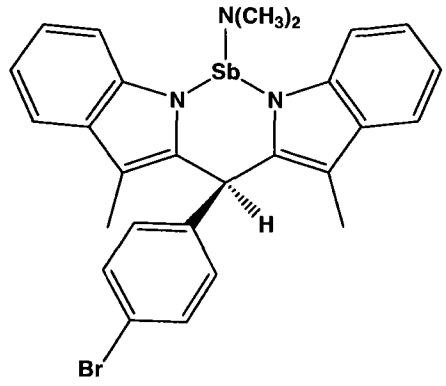


di-(3-methylindol-2-yl)chlorophosphine-4-fluorophenylmethane **5.3c** PCl_3 (0.050 mL, 0.57 mmol) was added dropwise to a solution of di-(3-methylindolyl)-4-fluorophenylmethane (0.189g, 0.440 mmol in 2 mL dichloromethane), followed immediately by addition of 0.140 g (1.15 mmol) DMAP. The resulting clear, reddish solution was allowed to stir for 72 hours before removal of the solvent *in vacuo*. The product was extracted with THF (3 x 1.5 mL), filtered through a glass frit and the solvent was removed *in vacuo*. The maroon solid was washed with n-hexanes (3 x 1.5mL) and diethyl ether (3 x 1.5mL) to yield product. $^{31}P\{^1H\}$ NMR(CD_2Cl_2, major isomer): δ = 86.1 ppm ^1H NMR(CD_2Cl_2, major isomer) : 2.42 (s, 6H, 2 C*H*$_3$), 5.94 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 7.15 (d, 2H, *H*Ar) 7.21 (d, 2H, *H*Ar), 7.31 (m, 4H, *H*Ar), 7.61 (d, 2H, *H*Ar), 7.68 (d, 2H, *H*Ar)



di-(3-methylindol-2-yl)dimethylamidoantimony-4-bromophenylmethane **5.7** $Sb[N(CH_{3)2}]$

To a Schlenk flask containing a suspension of 0.336g (0.783 mmol) di-(3-methylindolyl)-4-bromophenylmethane in 2 mL toluene cooled to -78° C in a dry ice/acetone bath was added a solution of 0.225g (0.88 mmol) tris(dimethylamido)antimony in 2 mL toluene. The resultant white suspension was allowed to warm to room temperature over a period of 3 hours, with stirring, by which point it had become a slightly cloudy, colourless solution. Volatiles were then removed *in vacuo* and the resulting white solid was washed with hexanes (2 x 1.5 mL) to yield **5.7**. (0.407g, 88% yield) ^{1}H NMR ($CDCl_3$): 2.48 (s, 6H, NC*H*$_3$), 2.77 (s, 6H, 2 C*H*$_3$), 5.84 [s, 1H C*H*(4-bromophenyl)(3-methylindolyl)$_2$], 6.69 (d of quartets, 2H, *H*Ar, $^3J_{HH}$ = 8.6 Hz), 7.16 (m, 4H, *H*Ar, $^3J_{HH}$ = 8.1 Hz),), 7.31 (m, 4H, *H*Ar, $^3J_{HH}$ = 7.9 Hz),), 7.63 (m, 2H, *H*Ar, $^3J_{HH}$ = 8.6 Hz) ^{13}C NMR ($CDCl_3$): 9.21 (*C*Me), 38.11 (NCH_3), 41.02 (*C*H(3-methylindolyl)$_2$), 110.95 (*C*Ar), 111.43 (*C*Ar), 118.68 (*C*Ar), 119.21 (*C*Ar), 119.60 (*C*Ar), 121.30 (*C*Ar), 121.84 (*C*Ar), 129.76 (*C*Ar), 131.46 (*C*Ar), 132.00 (*C*Ar), 137.04 (*C*Ar), 141.31 (*C*Ar) Anal. Calcd. For $C_{27}H_{25}BrN_3Sb$: C 54.67 H 4.35, N 7.08 Found: C 54.52 H 4.34 N 7.01



Structural determination of 5.3a

A single crystal was mounted on a thin glass fibre and held using viscous oil. It was subsequently cooled to the collection temperature. Crystal data and measurement details are summarized in **Tables 2.1** and **2.2**. Data was collected on a Bruker AX SMART 1k CCD diffractometer using 0.3o ω-scans at 0, 90 and 180 in ϕ. Unit-cell parameters were obtained from 60 frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied (Blessing, R. *Acta Cryst.* **1995**, *A51*, 33-38). Direct methods were used to solve molecular structures and connectivity, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.1 program library (Sheldrick, G.M., Bruker AXS, Madison, WI, 1997).

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Summary and Conclusions

The coordination chemistry of ligands featuring two indole moieties has been extended. Reactivity of two different varieties of bis(indolyl) ligands has been explored.

The lithium salt of a new di(3-methylindolyl)bicyclononylborate ligand has been synthesized and characterized using a facile, high-yield synthesis. The reactivity with various early transition-metal and main group halides has been explored with the goal of binding these metals to the π-system of the indole ligand to produce complexes which would be the first borate-bridged indolyl metallocenophane complexes. Although the ligand demonstrated reactivity with calcium, yttrium, zirconium, titanium, chromium, tantalum, tungsten and aluminum halides, the only product isolated and characterized from these reactions was a chromium complex where the bicyclononane was incorporated but the indole moieties were not, indicating the ligand had decomposed. These results indicate that new strategies may have to be employed in both the synthesis and isolation of transition metal complexes of di(3-methylindolyl)bicyclononylborate.

Extending the reactivity of known diindolylmethane ligands proved more successful. Previously, only complexes of titanium and zirconium were synthesized and definitively characterized using the diindolylmethane ligand; aluminum diindolylmethanes were postulated but not definitively characterized, and triindolylmethane phosphine complexes were known. This report has demonstrated that diindolylmethane can successfully support a variety of other main group centres, including metals from the s-block and elements from Groups 13 and 15.

Most investigations of diindolylmethane reported herein specifically employed the di(3-methylindol-2-yl)-4-bromophenylmethane. Hydrogen elimination reactions

yielded borane and alane complexes of this ligand. Reaction of Group 1 metal salts of monoanionic bases yielded the dilithium, disodium, and dipotassium salts of diindolylmethane. These are synthetically useful potential precursors to other diindolylmethane complexes through salt metathesis reactions, as demonstrated by reaction of the dipotassium salt with calcium iodide to yield a calcium diindolylmethane complex. Group 15 complexes synthesized include chloro- and bromophosphines of both di(3-methylindol-2-yl)-4-bromophenylmethane and di(3-methylindol-2-yl)-4-fluorophenylmethane. These Group 15 complexes in particular were used to investigate the Lewis acid/base properties of diindolylmethane complexes, as the nitrogen atoms should be weaker π-donors than ligands featuring nitrogen donors with non-aromatic lone pairs.

Some of these reactions did not result in the reactivity expected. Attempts to abstract the halide atom from the diindolylmethane halophosphine complexes were unsuccessful, despite using several different abstraction agents and procedures successfully employed in the synthesis of similar phosphenium cations. From these we learned that diindolylemethane has fundamental differences in reactivity from other chelating nitrogen ligands. Other reactions were aimed at complexes with fundamental differences from known structures. The calcium complex differed from related complexes in that the diindolylmethane ligand was a chelating, dianionic ligand, whereas previous related calcium(II) complexes had employed monanion chelating nitrogen ligands where one nitrogen was a dative donor, with an additional separate monanionic substituent at calcium. Other reactions did mimic established reactivity, but these too were useful, as the gradual extension of synthetic methods contributes to the overall body

of knowledge of these reactions, as well as indicates areas of reactivity in which diindolylmethane is similar to other ligands.

Although diindolylmethane is only one ligand in an infinite array of possible ligands, and its compounds are only a few of the infinite number of possible compounds in so-called chemical space, the exploration of its chemistry yieled other small pieces of synthetic chemistry knowledge. Most importantly, the processes by which these small pieces of knowledge were acquired were invaluable tools in the investigator's education.