Di(3-methylindolyl)methane complexes of aluminum and gallium alkyls

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A Thesis

Entitled

Di(3-methylindolyl)methane Complexes of Aluminum and Gallium Alkyls

By

Anirban Das

Submitted as a partial fulfillment of the requirements for

the Master of Science Degree in Chemistry

Advisor: Mark R. Mason, Ph.D.

Graduate School

The University of Toledo

August 2007
An abstract of

Di(3-methylindolyl)methane Complexes of Aluminum and Gallium Alkyls

Anirban Das

Submitted in partial fulfillment of the requirements for
the Master of Science Degree in Chemistry

The University of Toledo
August 2007

Di- and tri(3-methylindolyl)methanes have strong electron-withdrawing ability when η¹–N bound and reduced N→M π-donation since the nitrogen lone pair is delocalized over the aromatic system. This makes the resultant complex less prone to M–N–M bridging. Thus, complexes based on these frameworks are potentially ideal for generation of monomeric electrophilic metal centers. Moreover, the ligands can be modified to act as monoanionic, dianionic or trianionic ligands by variation of the substituents. This thesis reports the synthesis and characterization of complexes of aluminum and gallium alkyls with two ligands, di(3-methylindolyl)pyridylmethane (L¹H₂) and di(3-methylindolyl)(1-methylimidazolyl)methane (L³H₂).
Chapter 2 describes the reactions of $\text{R}_3\text{M}$ ($\text{R} = \text{^tBu}, \text{M} = \text{Al, Ga}; \text{R} = \text{Me}, \text{Et}; \text{M} = \text{Al}$) with di(3-methylindolyl)pyridylmethane ($\text{L}^1\text{H}_2$). Two bidentate complexes $\text{L}^1\text{HA}^t\text{Bu}_2$ (6) and $\text{L}^1\text{HG}^t\text{Bu}_2$ (7) were synthesized and characterized by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy. Additionally, 6 was characterized by X-ray crystallography and 7 by elemental analysis. In each complex, one of the indolyl moieties of the ligand is deprotonated and binds to the metal, whereas the other indolyl moiety is protonated and uncoordinated. The pyridyl moiety is coordinated to the metal. A tridentate complex $\text{L}^1\text{Ga}^t\text{Bu}$ (8) has also been synthesized and characterized by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy. In 8, the pyridyl moiety is coordinated to gallium and both indolyl moieties are deprotonated and bound to gallium. A previously reported bis-aluminum complex $\text{L}^1\text{Al}_2\text{Me}_4$ (3) was characterized by X-ray crystallography. The crystal structure revealed that the two aluminums of 3 are bridged by an $\eta^1$–N indolyl moiety of the ligand. The other indole moiety of the ligand is bound to one of the aluminums, while the pyridyl is coordinated to the other aluminum. This is the first reported example of a group 13 complex with a bridging $\eta^1$–N indolyl group. The bis-aluminum complex $\text{L}^1\text{Al}_2\text{Et}_4$ (9) was also synthesized and characterized by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy and elemental analysis. The NMR spectroscopic data of 9 indicated that its structure is analogous to that of 3.

Chapter 3 describes the synthesis of di(3-methylindolyl)(1-methylimidazolyl)methane ($\text{L}^2\text{H}_2$) as well as its reactions with $\text{R}_3\text{M}$ ($\text{R} = \text{Me, Et, }\text{^tBu, }\text{Bu; M} = \text{Al; R} = \text{^tBu, M} = \text{Ga}$). A series of bidentate complexes $\text{L}^2\text{HA}^t\text{R}_2$ ($\text{R} = \text{Me (2a), Et (2b), }\text{^tBu (2c), }\text{Bu (2d)}$) and $\text{L}^2\text{Ga}^t\text{Bu}_2$ (3) were synthesized and characterized by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy. Compounds 2d and 3 were characterized by X-ray crystallography and 2b, 2c and 3 by elemental analysis. Analogous to bidentate complexes of $\text{L}^1\text{H}_2$ discussed in chapter 2, one of the indolyl moieties of the ligand in 2a-d and 3 is deprotonated and binds to the metal whereas the other indole is protonated and
The N-methylimidazolyl moiety is coordinated to the metal. Crystallographically, complexes 2d and 3 were found to be isomorphous. Two bis-aluminum complexes $\text{L}_2\text{Al}_2\text{Me}_4$ (4a) and $\text{L}_2\text{Al}_2\text{Et}_4$ (4b) were synthesized and characterized by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy. Additionally, 4b was characterized by elemental analysis. The NMR spectroscopic data indicate that the two indolyl moieties on the ligand, as well as the four alkyl groups, two each on the two aluminums, are chemically inequivalent. On the basis of NMR spectroscopic data, the structures of complexes 4a and 4b were proposed to be analogous to those for bis-aluminum complexes 3 and 9 discussed in chapter 2.
This thesis is dedicated to

My parents Mr. Arun Kumar Das and Mrs. Reba Das

My wife Papiya
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</tr>
<tr>
<td>CCD</td>
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<tr>
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<td>Chloroform-d</td>
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Chapter One

Review of Complexes of Aluminum and Gallium Alkyls with Nitrogen-Donor Ligands

1.1 Introduction

Complexes of aluminum and gallium alkyls with nitrogen-donor ligands are widely being investigated for use in organic synthesis and catalysis. The Lewis acidic nature of the metal atom allows these complexes to act as catalysts for various reactions like polymerization of ethylene.\(^1\) They can also function as cocatalysts for many processes\(^2\) like the polymerization of ethylene. Air- and moisture-sensitive reaction techniques have to be used for the preparation of aluminum–nitrogen bonded complexes due to the oxophilic nature of aluminum and the Al–N bond being prone to hydrolysis.

Cationic complexes of aluminum are of interest because of the enhanced Lewis acidity of the aluminum center versus that of the neutral analogs.\(^1\) Low-coordinate aluminum cationic species are more electrophilic. The stability of the complex formed depends on both the counter anion as well as the ligand. Lewis bases such as NMe\(_2\)Ph\(^3\) are used to stabilize the formed cationic aluminum alkyls.

Complexes of aluminum and gallium alkyls with some of the most common nitrogen-donor ligands are reviewed in the following sections. Emphasis shall be placed on the aluminum and gallium complexes of ligand systems containing indole, carbazole
and pyrrolyl moieties as these are closely related to the ligands and their complexes discussed in the later chapters of this thesis. Heterometallic complexes are excluded from the scope of this review. Cationic aluminum complexes as well as Salen complexes of group 13 elements have been extensively reviewed by Atwood. The complexes discussed in those reviews have also been excluded in this discussion. A comprehensive review on structurally characterized organoaluminum compounds, including those with N-donor ligands, reported prior to 1997, and classification and analysis of their crystallographic and structural data has been carried out by Holloway and Melnik. Another good source of information is the Encyclopedia of Inorganic Chemistry. A detailed discussion on the coordination chemistry of aluminum and its complexes synthesized prior to 1993 is also available. The complexes discussed in these sources have also been omitted from the scope of the current discussion for the sake of conciseness.

1.2 Monodentate Complexes and Adducts

Aluminum and gallium alkyls are strong Lewis acids, hence they readily form acid-base adducts with simple nitrogen donors (eq 1). The chemistry of the simple adducts has been reviewed in the classic text by Mole. The first adduct of trimethylaluminum was observed by Mole in 1966. On reacting di-iso-butylaluminum hydride with Ph–HC=N–Ph in benzene

\[
\text{R}_3\text{Al} + \text{:Base} \rightarrow \text{R}_3\text{Al} \leftrightarrow \text{Base}
\]

Base = NR_3, pyridine, N=CR
in less than 14% yield. Though there are numerous examples of such adducts, as a recent representative example, Schultz\textsuperscript{9,10} and co-workers synthesized 4-dimethylaminopyridine adducts with MMe\textsubscript{3} (M= Al, Ga, In).

One of the major reasons for interest in such adducts is that they can potentially act as precursors to nitrides of aluminum and gallium. The nitrides of aluminum, gallium and indium as well as their mixed alloys Al\textsubscript{x}Ga\textsubscript{y}In\textsubscript{1-x-y}N can be used in micro and opto-electronic devices like the blue and UV laser diodes for high density optical storage.\textsuperscript{11} Metal organic chemical vapor deposition (MOCVD) techniques are used to deposit thin films of group 13 metal nitrides. The starting materials for this process are R\textsubscript{3}M (R= Me, Et; M = Al, Ga, In) and a large excess of ammonia. Several studies have therefore been directed to synthesize precursors of group 13 nitrides. Gal and co-workers\textsuperscript{12} synthesized the first example of an adduct of aziridine and a group 13 metal. The general formula is Me\textsubscript{3}M•LH, where M = Al or Ga and LH = 1, 2, 3.

\[
\begin{align*}
\text{1} & \quad \text{2} & \quad \text{3}
\end{align*}
\]

Interrante\textsuperscript{13} and co-workers reacted trimethylaluminum and tri-\textit{tert}-butylaluminum with ammonia in hydrocarbon solvents at high temperatures to afford trimeric species [(CH\textsubscript{3})\textsubscript{2}AlNH\textsubscript{2}]\textsubscript{3} and [(C\textsubscript{4}H\textsubscript{9})\textsubscript{2}AlNH\textsubscript{2}]\textsubscript{3}, respectively. It may be noted that further reaction results in the formation of cage iminoalanes of the formula [RAINH]\textsubscript{n} (n = 4, 5, 6, 7, 8).\textsuperscript{7} Cowley\textsuperscript{14} and co-workers noted that high temperatures used in MOCVD results in loss of stoichiometry due to nitrogen deficiency and introduces thermal stress on the resulting films, therefore single source precursors to MN (M = Al, Ga, In) were
necessary to reduce thermal costs. With the aim of developing such precursors they synthesized \((\text{Me}_2\text{NH})\text{Al}-(\text{pyrrolyl})_3\), 4. Schumann\(^{15}\) and co-workers also working to develop such precursors have synthesized intramolecularly stabilized organoaluminum and organogallium alkoxides, 5. Though alkoxides have an O–M bond there is a N→M dative bond, hence they are being discussed here merely as a representative example. Gibson\(^{16}\) and co-workers, also investigating precursors to aluminum nitrides, synthesized aluminum-containing ring systems 6, analogous to calix[4]pyrrole. Uhl has synthesized dimeric dialkyl aluminum\(^{17}\) and gallium\(^{18}\) hydrazines as potential precursors to aluminum and gallium nitrides.

Apart from developing precursors to aluminum and gallium nitrides, there are several other reasons for investigating adducts and monomeric complexes of aluminum and gallium. Roesky,\(^{19}\) with the aim of investigating complexes for polymerization of ethylene using single-site catalysts, synthesized mono(1-aza-allyl) complexes of aluminum. Koten\(^{20}\) and co-workers, while studying the reactivity of \(\alpha\)-imino ketones with triorganoaluminum reagents synthesized coordination products \[[(\text{AlR}_3)_2\{\sigma\text{-N or }\sigma\text{-O-} (R^1\text{N}=C(R^2)C(R^3)=O)\}] \] and \[[(\text{AlR}_3)_2\{\sigma,\sigma\text{-N,O-} (R^1\text{N}=C(R^2)C(R^3)=O)\}] \]. They also synthesized diorganoaluminum(\(\alpha\)-imino)alkoxides and diorganoaluminum enolates. These types of complexes were candidates for studies to develop new routes for chemo-
and regio-selective conversion of heterobutadienes by organoaluminum reagents. Mitzel,\textsuperscript{21} investigating simple systems containing the M–C–N (M = group 2, 3 metal atom) linkage to develop complexes with geminal donor and acceptor site in the same molecule, for achieving characteristic reactivity, reported the synthesis of \((\text{Me}_2\text{MCH}_2\text{NMe}_2)_2\) (M = Al, Ga).

Wang and coworkers\textsuperscript{22} reported the synthesis of compounds (e.g. 7) resulting from the reaction of 7-azaindole with trialkylaluminum. The blue luminescent properties of deprotonated 7-azaindole (7-azain) have potential application in electroluminescent display devices. These compounds display a blue luminescence and an improved stability towards air and moisture in comparison with related dinuclear and polynuclear compounds. Tri(8-quinolinolato)aluminum (Alq\textsubscript{3}) is one of the most widely used complexes for organic light-emitting devices because it is a green emitter and an efficient electron-transporting material.

\[
\begin{align*}
\text{N} & & \text{N} & & \text{N} \\
\text{N} & & \text{Al} & & \text{N} \\
\text{N} & & \text{N} & & \text{Al} \\
\text{N} & & \text{N} & & \text{N}
\end{align*}
\]

\(7\)

\[
\begin{align*}
\text{N} & & \text{N} & & \text{N} \\
\text{N} & & \text{N} & & \text{Al} \\
\text{N} & & \text{N} & & \text{N} \\
\text{N} & & \text{N} & & \text{N}
\end{align*}
\]

\(8\)

\(R = \text{Me, Et}\)

Gibson\textsuperscript{23} noted that there was low polymerization activity of olefins by using cationic alkylaluminum species involving bi- and tridentate N-donor ligands, where the active species was assumed to be three- or four-coordinate, respectively. He cited the work of Budzelaar, who by computational studies, inferred that barriers to ethylene
polymerization may be too high to allow efficient chain propagation. They therefore investigated aluminum pre-catalysts of the type \( \text{R'}_2\text{NAIR}_2 \), 8, where the amide is a stearically hindered carbazolide ligand, 1,8-diphenyl-3,6-dimethylcarbazole. The bulky amide can potentially stabilize mononuclear three-coordinate pre-catalysts and two-coordinate cationic alkyl species of the type \([\text{R'}_2\text{NAIR}]^+\). He isolated and characterized monomeric complexes with three-coordinate aluminum centers. Smith\(^{24}\) and co-workers have synthesized bisaluminum complexes bridged by pyrrolidine (9) and piperidine (10) moieties. The Mason group\(^{25}\) achieved polymerization of epichlorohydrin using di(3-methylindolyl)phenylmethane.

\[ \text{NNN} \quad \text{NNN} \quad \text{NNN} \quad \text{NNN} \quad \text{NNN} \]

\[ 9 \quad 10 \]

### 1.3 Bidentate Complexes

Monoanionic bidentate nitrogen-donor ligands can form complexes with both main group and transition metals. Some representative examples of such ligands are provided in Scheme 1. Atwood\(^{26}\) and coworkers noted that complexes of group 13 elements with bidentate nitrogen-donor ligands can be broadly classified into six general categories (Scheme 2), having one (a), two (c), and three (d) carbon atoms separating
Scheme 1. Examples of some monoanionic bidentate N-donor ligands

the two nitrogen atoms. They also noted that for N and O mixed-donor ligands two (e) and three (f) carbon atoms are most prevalent.

Salicylaldiminato and pyrolylaldiminato are some more examples of such ligands. The chelating pyrolylaldiminato ligand forms five-membered ring systems with

Scheme 2. General types of group 13 compounds with bidentate nitrogen-containing ligands
metal ions, while salicylaldiminato ligands tend to form six-membered rings (Scheme 3). Liang\textsuperscript{27} and Roesky\textsuperscript{28} have reported the synthesis of pyrrolylaldiminato complexes \textbf{11} and \textbf{12}, respectively, of aluminum.

\begin{center}
\textbf{Scheme 3.} Representative pyrrolylaldiminato complexes (left) and salicylaldiminato complexes (right). R= H, \textsuperscript{1}Bu; M = Al.
\end{center}

Several substituted pyrrole ligands can also be categorized as bidentate nitrogen donors. Huang and co-workers have synthesized bidentate\textsuperscript{29} complex \textbf{13} of a substituted pyrrole ligand. Subsequently they achieved insertion of phenylisocyanate into the Al–N bond, resulting in C–N bond activation.\textsuperscript{29} Isocyanates serve as useful models for studying the chemical behavior of carbon monoxide, although little research in main group
chemistry is focused on binding and activation of carbon monoxide.\textsuperscript{30}

Pyrazolato and 2-pyridine carboxyaldehyde phenyl hydrazone ligands can also form bidentate complexes with aluminum and gallium. Roesky\textsuperscript{31} and co-workers have synthesized $\mu$-$\eta^1$, $\eta^1$-3,5-di-\textit{tert}-butylpyrazolato derivatives (14) of aluminum. Winter\textsuperscript{32} and co-workers have synthesized many monometallic and bi-metallic (analogous to 14) pyrazolate complexes of aluminum (e.g. 16 and 17). He has also synthesized pyrazolate bridged digallium complexes.\textsuperscript{33} Kang\textsuperscript{34} and co-workers have synthesized aluminum and gallium complexes of 2-pyridine carboxyaldehyde phenyl hydrazone, 15.

Complexes of aluminum alkyls with other bidentate nitrogen-donor ligands have also been reported. Lee\textsuperscript{35} and co-workers, with the aim to synthesize and screen potential single-site polymerization catalysts have reported the synthesis of pyridineenolato, 18, and pyridineenamido complexes of aluminum. Gibson\textsuperscript{36} and coworkers, on reaction of the pyridyl-imine [ArN=CH–2–py] (Ar = 2,6-\textit{i}Pr$_2$C$_6$H$_3$) with trimethylaluminum synthesized a racemic mixture of two enantiomers of aluminum pyridyl amide complex [AlMe$_2$\{ArN–CH(Me)–2–py\}], 19. The geometry at the aluminum is distorted tetrahedral with angles ranging from 84.5(1)$^\circ$ to 121.8(1)$^\circ$, the former angle corresponding to the bite
of the chelating ligand. The five-membered metalcyclic ring is slightly folded with the aluminum atom lying 0.24 Å out of plane of the other four atoms.

Another important class of bidentate nitrogen-donor ligands are β-diketiminates. β-Diketiminate complexes adopt a range of coordination modes and can stabilize low oxidation states. The chemistry of these ligands has been recently reviewed by Lappert and co-workers. Some recent representative examples are provided here. Huang and co-workers have synthesized β-diketiminate complexes of aluminum alkyls. A structure of such a complex is discussed later in this chapter. They achieved ring-opening polymerization of ε-caprolactone with these complexes.
Power \(^{39}\) had reported \(\beta\)-diketiminate ligands with electron-withdrawing groups. Cowley and coworkers\(^{40}\) synthesized aluminum and gallium complex 20 with \(C_6F_5\) substituted \(\beta\)-diketiminate ligands. Roesky\(^{41}\) and co-workers have also synthesized a series of aluminum complexes containing \(C_6F_5\) substituted \(\beta\)-diketiminate ligands.

There are several nitrogen-containing mixed donor bidentate ligands, a few representative examples shall be discussed here. Dagorne\(^{42}\) and co-workers have focused their attention on developing O,N-bidentate aluminum alkyl cations as potential olefin polymerization catalysts and have synthesized neutral and cationic alkylaluminum complexes with aminophenolate ligands (21). Wang\(^{43}\) and co-workers reported the synthesis of a new functionalized iminophosphorane ligand, \(\text{Ph}_2\text{P}(8-\text{CH}_2\text{C}_6\text{H}_5\text{N})=\text{N}^{\text{tBu}}\))
(C₉H₈N = quinolyl). Reaction of these with trimethylaluminum yielded the aluminum iminophosphorano(2-methyl-8-quinolyl)methanediide complexes, 22.

There are several reports of complexes of aluminum alkyls with amidinates. Arnold and Schmidt⁴⁴ have summarized the various amidinate ligands employed to form monoamidinate complexes. They synthesized a neutral aluminum complex with a bulky amidine and achieved alkyl abstraction by using trityl salts to generate the cationic aluminum species 23. Barry and coworkers⁴⁵ synthesized various aluminum amidinates as precursors to atomic layer deposition. Cameron⁴⁶ and coworkers have synthesized complexes of aluminum alkyls with m-terphenyl substituted amidinates.

Other ligands whose bidentate complexes with aluminum alkyls are known are aminotroponinate,⁴⁷ N,N’-dimethylpiperazines,⁴⁸ imino-amide⁴⁹ and aminobis(pyrroyzoly).⁵⁰ Yamamoto⁵¹ and coworkers working towards development of Alq₃ precursors synthesized AlEtq₂ complexes, 24. Yamamoto⁵² also used aluminum bis(trifluoromethylsulfonyl) amides as a versatile catalyst for C–C bond formations.
1.4 Tridentate complexes

Aluminum and gallium alkyls are known to form various tridentate complexes with nitrogen-donor ligands. Mason and coworkers\textsuperscript{53,25} have synthesized di- and tri-(3-methylindolyl)methane complexes with aluminum and gallium. Huang\textsuperscript{54} and coworkers synthesized tridentate complexes, 25, of substituted pyrrole ligands. Budzelaar\textsuperscript{55} and coworkers synthesized complexes of aluminum alkyls with variations of the diimine pyridine ligands, 26. Brookhart\textsuperscript{56} and Gibson\textsuperscript{57} had previously demonstrated that complexes of these types of ligands with iron and cobalt are effective olefin oligomerization and polymerization catalysts.

![Complex 25](image)

![Complex 26](image)

Ar = 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>

1.5 Tetradentate complexes

One of the most important classes of ligands in this category are the tren ligands. These have been extensively reviewed by Verkade.\textsuperscript{58} A representative complex of aluminum with the tren ligand alumatrane is provided, 27. Azaaluminatranes (E = NR)
are being investigated as precursors to AlN and can adopt four- or five-coordinate geometries.\textsuperscript{59}

Metal complexes of Schiff bases and related ligands like Salen are very important in coordination chemistry.\textsuperscript{4} In these complexes the reactivity can be fine-tuned by modifying the coordination environment at the metal center by varying the substituents on the ligands. Complexes of such ligands with aluminum are known to catalyze the polymerization of ethylene\textsuperscript{60} and methacrylate\textsuperscript{61} and also the ring-opening methathesis polymerization\textsuperscript{62} of heterocyclic monomers. Salophen ligands are o-phenylenediamine bridged analogs of the Salen ligands. Goedken\textsuperscript{63} and coworkers have synthesized aluminum complexes of ACEN, SALEN, SALPN AND SALOPHEN ligands (Scheme 4). Since the radius of aluminum is comparable to that of high-valent first row transition metals, they expected that aluminum should have a good fit into centers of chelate rings. They further expected the properties of the aluminum chelate complexes formed to be similar to those for first row transition metals based on charge and size. They observed that the reactivity of the complex depends on the rigidity of the backbone, with SALOPHEN being the most reactive and SALPN being the least reactive.

Lewinski\textsuperscript{64} and co-workers on reacting N-phenylsalicylideneimine (HsaldPh) with \textit{M}Me\textsubscript{3} (\textit{M} = Al, Ga, In) obtained O,N-chelate complexes MeM(saldPh)\textsubscript{2} (28). The aluminum complex undergoes ligand redistribution in $\gamma$-picoline to form the five-
coordinate complex MeAl(saldPh)$_2$, while the gallium and the indium complexes are stable. The complexes were characterized by X-ray crystallography and $^{27}$Al NMR spectroscopy.

![Scheme 4](https://example.com/scheme4.png)

**Scheme 4.** Schiff-base aluminum alkyl complexes.

Aza-crown ethers also fall in the category of tetradentate ligands. These have been extensively reviewed.$^7$ A representative azacrown ether complex, 29, synthesized by Robinson$^6$ and coworkers, where the penta-coordinate aluminum atom is in a trigonal-bipyramidal environment is provided.

![29](https://example.com/29.png)

29
1.6. Indole, Carbazole and Pyrrole Bridging Complexes of Main Group Metals

Wang and coworkers synthesized dinuclear aluminum (30) and boron complexes bridged by 7-azaindole (31) moieties. As discussed earlier for similar mononuclear complexes, these molecules have potential application in electroluminescent display devices. They reported the application of $^{27}$Al multiple-quantum-magic-angle-spinning (MQMAS) spectroscopy to identify disorder of two blue luminescent organoaluminum compounds in the solid state.

Klingbiel and co-workers synthesized a bimetallic lithium complex with bridging N-indolyl moieties. Schleyer and coworkers synthesized N-carbazole bridged dimeric lithiocarbazole, cesiocarbazole and potassiocarbazole. They also synthesized N-indolyl bridged dimeric lithioindole and sodioindole complexes. Kuhn and co-workers synthesized 2,3,4,5-tetramethyl-1-sodiopyrrole with the pyrrole bridging in both $\eta^1$ and $\eta^5$ mode. Weidlein and co-workers synthesized bimetallic aluminum and gallium complexes with C-bridging N-methyl pyrroles and C-bridging pyrrolidines. Bock and co-workers deprotonated carbazole by sodium metal mirror and achieved Na$^+$ coordination numbers 3 to 7. Evans and co-workers have synthesized a 2,3-dimethylindole complex with potassium, in which the dimethylindole anion binds and
bridges potassium ions in three different binding modes, $\eta^1$, $\eta^3$ and $\eta^5$ to form a two-dimensional extended structure. Jackman$^{26}$ and co-workers have synthesized dimeric lithium complexes with N-bridging indoles.

1.7 Research statement

From the preceding sections it is evident that complexes of aluminum and gallium alkyls with nitrogen-donor ligands have tremendous potential for application in various synthetic processes as catalysts, co-catalysts and precursors to new materials. Also evident in this mini-review is the paucity of pyrrolyl, indolyl and carbazolyl complexes of aluminum. This is noteworthy since $\eta^1$–N bound indole-based ligand frameworks have strong electron-withdrawing ability and reduced N→M $\pi$-donation since the nitrogen lone pair is delocalized over the aromatic system. This makes the resultant complex less prone to M–N–M bridging. Thus, complexes based on indole-containing frameworks such as di- and tri(3-methylindolyl)methanes are potentially ideal for generation of electrophilic metal centers. Moreover, these ligands can be modified to act as monoanionic, dianionic or trianionic ligands by variation of the substituents. Therefore, the chemistry of these ligand systems merit further investigation particularly in the context of generating strong group 13 Lewis acids.

This thesis reports on the products obtained from reactions of aluminum and gallium alkyls with di-(3-methylindolyl)methanes. Chapter 2 describes the synthesis and characterization of bidentate dialkylaluminum and dialkylgallium complexes of di(3-methylindolyl)pyridylmethane. A tridentate monoalkylgallium complex, as well as $\eta^1$–N–3-methylindole bridging bimetallic complexes are also described. Chapter 3 describes the
synthesis and characterization of a series of bidentate dialkylationuminum complexes of di(3-methylindolyl)(1-methylimidazolyl)methane. It also describes the synthesis and characterization of $\eta^1$–N–3-methylindole bridging bimetallic complexes with the same ligand.

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Chapter Two

Synthesis and Characterization of Di(3-methylindolyl)pyridylmethane Complexes of Aluminum and Gallium

2.1 Introduction

The discovery by Jordan\textsuperscript{1} that ethylene can be polymerized under mild conditions using three-coordinate cationic aluminum complexes with diketiminate ligands has led to much research on the synthesis and properties of low-coordinate, highly Lewis acidic group 13 complexes. Fneich and Mason\textsuperscript{2} previously worked to develop complexes of group 13 metals with 3-methylindole-based bidentate and tridentate nitrogen-donor ligands. Their aim was to generate Lewis acidic three-coordinate cationic complexes via alkyl abstraction from neutral four-coordinate aluminum and gallium complexes, and then screen them for a variety of purposes such as ethylene polymerization and binding of carbon monoxide.

Indole-based ligands are of interest since the lone pair of electrons on the indole nitrogen is delocalized in the aromatic framework.\textsuperscript{3} This reduces the N→M π-donation, thus increasing the Lewis acidity of the metal. Indoles also exhibit a reduced tendency for M–N–M bridging thus favoring formation of monomeric complexes. The indole derivative of interest is 3-methylindole. The C3 position in indole is most susceptible to
electrophilic attack, therefore if this position is protected an electrophile is favored to attack C2. This makes 3-methylindole a suitable molecule on which to base the ligand framework.

Fneich reported the synthesis of $1$, the geometry of which allows it to form stable complexes with six-membered chelate rings. Fneich synthesized a series of monoalkyl aluminum complexes in which deprotonated ligand $1$ adopts a tridentate coordination mode (eq 1). It was observed that the yield of $2d$ was very low. In addition it was observed that for the reaction of $1$ with trimethylaluminum, stoichiometry plays an important role. Use of more than one equivalent of trimethylaluminum per equivalent of $1$ resulted in the formation of a mixture of $2a$ and a bimetallic species $3$ of formula $\text{LA} \text{Al}_{2}\text{Me}_4 (\text{LH}_2 = 1)$. Complex $3$ was characterized by NMR spectral data. The $^1\text{H NMR}$

$$\begin{align*}
\text{H}_3\text{C} & \quad \text{NH} \\
\text{H}_3\text{C} & \quad \text{NH} \\
\text{H}_3\text{C} \\
\text{H}_3\text{C} \\
\text{AlR}_3 \\
\end{align*}$$

toluene
$15\text{ h, }20\,^\circ\text{C}$

$$\begin{align*}
\text{Al} & \quad \text{H}_3\text{C} \\
\text{H}_3\text{C} & \quad \text{AlR}_3 \\
\text{H}_3\text{C} & \quad \text{H}_3\text{C} \\
\end{align*}$$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$R$</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2a$</td>
<td>Me</td>
<td>91%</td>
</tr>
<tr>
<td>$2b$</td>
<td>Et</td>
<td>72%</td>
</tr>
<tr>
<td>$2c$</td>
<td>$^1\text{Bu}$</td>
<td>47%</td>
</tr>
<tr>
<td>$2d$</td>
<td>$^1\text{Bu}$*</td>
<td>19%</td>
</tr>
</tbody>
</table>

* sluggish at $20\,^\circ\text{C}$, brought to reflux

spectrum indicated two sets of resonances for the protons attached to the two indole groups on the ligand framework. The resonances in both the aromatic and aliphatic region
corresponding to the two indoles were broad indicating that these were chemically inequivalent and exchanging at room temperature. Four distinct singlets upfield of TMS, each integrating to three protons, were also observed for the four methyl groups attached to the two aluminums. At room temperature two of these resonances were sharp indicating that they were rigidly bound to the aluminum, and two resonances were broad indicating fluxionality. The pyridyl resonances were relatively sharp, thus the aryl group is held rigidly. This leads to the two methyl groups on the aluminum being asymmetrically positioned between the indolyl rings resulting in the molecule being chemically inequivalent. Only one resonance at 6.25 ppm in the region corresponding to the methine proton was observed indicating the presence of a single complex. The $^{13}$C NMR spectrum similarly yielded four different resonances for each of the methyl carbons bound to aluminum. These resonances were broad due to quadrupolar broadening by aluminum-27 ($I = 5/2$). The $^{13}$C NMR spectrum also had two sets of resonances due to the different chemical environments of the two indole rings in the ligand backbone. Only one resonance was observed in the methine region of the spectrum at 41.25 ppm. The $^1$H and $^{13}$C NMR spectroscopic data were consistent with two possible structures, 3a and 3b.
To elucidate the actual structure of 3, COSY and NOESY\(^4\) were performed. \(^1\)H COSY (Co-relation spectroscopy) generates cross peaks corresponding to the resonances of protons attached to the adjacent carbons thus indicating connectivity in the molecule. NOESY (Nuclear Overhauser Effect Spectroscopy) provides through-space coupling information, thus indicating spatial proximity of hydrogen atoms. The schematic representation of the coupling information Fneich obtained from the NOESY spectrum is shown in Figure 2.1. On the basis of the above experiments Fneich proposed structure 3a. Variable-temperature \(^1\)H NMR (400 MHz) spectral data showed that coalescence of the two methyl peaks on aluminum takes place between 65 and 70 °C. Calculations yielded \(\Delta G_c^\ddagger\) of 15.1 ± 0.1 kcal/mol. For the indolyl methyl resonances coalescence takes place between 50 and 55 °C. \(\Delta G_c^\ddagger\) was calculated to be 15.5 ± 0.1 kcal/mol. The indolyl methyls were inequivalent since there is no plane of symmetry in the molecule. Though the pyridyl moiety lies in the plane bisecting the two indolyls, on constructing a model, it is seen that the methyls are oriented such that, the molecule overall is not symmetric.

![Figure 2.1](image-url)

**Figure 2.1.** Coupling information obtained from NOESY spectrum of 3.
Fneich also obtained tetramer 4, which presumably was the result of hydrolysis of 2b and 2c during recrystallization attempts. Complex 4, which was characterized crystallographically (Figure 2.2), exhibited chelation to each aluminum via pyridine and one of the indole rings. The second indole ring per ligand was uncoordinated.

![Molecular structure of complex 4.](image)

**Figure 2.2.** Molecular structure of complex 4.

The ultimate goal of Fneich’s work was to investigate the abstraction of an alkyl group from complexes such as 2a-d to generate a cationic aluminum complex 5. The vacant coordination site on aluminum should be highly Lewis acidic and may bind a variety of substrates, including CO, for novel chemical transformations.

![Cationic aluminum complex 5.](image)

We set out to elaborate upon the work of Fneich and further elucidate the structure of 3, explain the low yield reported for 2d, and also investigate if there were
other complexes in this system in which ligand 1 coordinates in a bidentate manner similar to that in 4. We also aimed to evaluate the use of 1 for preparing analogous complexes of gallium. Herein we report the preparation and characterization of previously unobserved bidentate complexes 6 and 7 as well as the tridentate gallium complex 8. We also confirm by means of X-ray crystallographic data that the structure of complex 3 was neither 3a or 3b, but a bis-dimethylaluminum species bridged by an N-indolyl moiety of ligand 1. The synthesis of the ethyl analog, LAl₂Et₄ (9) of the bimetallic complex 3 is also reported here.
2.2 Experimental Section

General Procedures. All reactions were performed under an atmosphere of purified nitrogen using standard inert atmosphere techniques. Hexanes and acetonitrile were distilled from calcium hydride and toluene was distilled from sodium. Chloroform-$d$ and benzene-$d_6$ were dried by storage over activated molecular sieves. Trimethylaluminum (2.0 M in toluene), triethylaluminum (neat), triisobutylaluminum (neat), 3-methylindole, pyridine 2-carbaldehyde, Amberlite IRA-67 ion exchange resin and anhydrous aluminum chloride were purchased from Aldrich Chemical. Tri-tert-butylaluminum was prepared by modification of the procedures reported by Lehmkuhl\textsuperscript{5a,b} and Uhl.\textsuperscript{5c} Tri-tert-butylgallium was prepared using the procedure reported by Kovar\textsuperscript{6} and co-workers. Di(3-methylindolyl)-2-pyridylmethane was prepared by modifications to the method described by Fneich.\textsuperscript{2} Solution NMR spectra were recorded on a Varian Unity 400 or Varian Inova 600 spectrometer. Two-dimensional NMR spectra were obtained on a Varian Inova 600 spectrometer. Chemical shifts are reported relative to tetramethylsilane. Some of the $^{13}$C NMR assignments are tentative and based on previously reported NMR assignments for diindolylmethanes,\textsuperscript{2,7} as well as NMR assignments of indole derivatives reported by Park.\textsuperscript{8} The numbering scheme for the pyridyl and indole rings of compound 1 is shown in Figure 2.3. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. High-resolution mass spectrometric analysis (TOF ES) was provided by the Mass Spectrometry and Proteomics Facility at The Ohio State University.
Figure 2.3. Numbering scheme for 1

Synthesis of (2-C\textsubscript{5}H\textsubscript{4}N)HC(3-CH\textsubscript{3}C\textsubscript{8}H\textsubscript{4}NH\textsubscript{2}) (1)

This procedure is a modification of that reported by Fneich.\textsuperscript{2} In the modified procedure, less solvent and Amberlite IRA-67 ion exchange resins are used. The previously reported NMR spectroscopic data for 1 is re-reported here for the convenience of the reader. Complete characterization of 1, including elemental analysis and crystallographic data is reported in the dissertation by Fneich.\textsuperscript{2} Amberlite IRA-67 (30 mL, 48 meq.) was added to a stirred suspension of [1\textbullet H][HSO\textsubscript{4}] (4.3 g, 0.024 mol) in 100 mL of acetonitrile and the mixture was stirred at 25 °C under nitrogen flow for 1 h resulting in a clear yellow solution. The Amberlite was filtered off and solvent was removed from the filtrate in vacuo resulting in a powdery, yellow solid 1. Yield: 3.2 g, 94%. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 600 MHz): \textit{δ} 9.05 (s, 2H, NH), 8.69 (d, \textsuperscript{3}J\textsubscript{HH} = 4.8 Hz, 1H, pyridyl H8), 7.68 (t, \textsuperscript{3}J\textsubscript{HH} = 7.8 Hz, 1H, pyridyl H9), 7.48 (d, \textsuperscript{3}J\textsubscript{HH} = 7.8 Hz, 2H, indolyl H7), 7.43 (d, \textsuperscript{3}J\textsubscript{HH} = 7.8 Hz, 1H, pyridyl H11), 7.29 (d, \textsuperscript{3}J\textsubscript{HH} = 7.8 Hz, 2H, indolyl H4), 7.22 (t, \textsuperscript{3}J\textsubscript{HH} = 7.4 Hz, 1H, pyridyl H10), 7.11 (t, \textsuperscript{3}J\textsubscript{HH} = 7.5 Hz, 2H, indolyl H5), 7.06 (t, \textsuperscript{3}J\textsubscript{HH} = 7.5 Hz, 2H, indolyl H6), 5.92 (s, 1H, CH), 2.32 (s, 6H, CH\textsubscript{3}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (CDCl\textsubscript{3}, 100.6 MHz): \textit{δ} 159.87 (s, pyridyl-\textit{ipso}), 149.67 (s, pyridyl C8), 137.60 (s, pyridyl C9), 135.36 (s, indolyl C7a), 133.10 (s, indolyl C2), 128.97 (s, indolyl C3a),
123.64 (s, pyridyl C10), 122.20 (s, pyridyl C11), 121.55 (s, indolyl C5), 119.12 (s, indolyl C6), 118.42 (s, indolyl C7), 110.86 (s, indolyl C4), 107.40 (s, indolyl C3), 41.61 (s, CH), 8.64 (s, CH₃). HRMS (ES) m/z for C₂₄H₂₂N₃ (M+H⁺): calcd, 352.1813; found, 352.1815.

**Synthesis of (2-C₅H₄N)HC(3-CH₃C₆H₄N)₂Al₂(CH₃)₄ (3)**

Complex 3 was prepared in an analogous procedure to that reported by Fneich, with the modification that the reaction mixture was stirred at 25 °C for 2 h instead of 50 °C for 48 h. Two equivalents of trimethylaluminum (1.0 mL, 2.0 mmol, 2.0 M solution in toluene) were added via syringe to a suspension of one equivalent of 1 (0.351 g, 1.00 mmol) in toluene (15 mL). An immediate color change to orange was noticed. The resulting solution was stirred at 25 °C for 1.5 h. The solution was then reduced to 2-3 mL in vacuo and hexanes (30 mL) were added while stirring. The solution was stored at –30 °C overnight. X-ray quality crystals were obtained, mounted on the diffractometer and the structure was elucidated based on the crystallographic data obtained. ¹H NMR (CDCl₃, 600 MHz): δ 8.30 (d, 3JHH = 4.8 Hz, 1H, pyridyl H8), 7.97 (t, 3JHH = 7.5 Hz, 1H, pyridyl H9), 7.87 (d, 3JHH = 8.4, 1H, pyridyl H11), 7.74 (br s, 1H, indolyl), 7.53 (br s, 1H, indolyl), 7.48 (br s, 1H, indolyl), 7.43 (t, 3JHH = 6.3 Hz, 1H, pyridyl H10), 7.41 (br s, 1H, indolyl), 7.36 (br s, 2H, indolyl), 6.99 (br s, 2H, indolyl), 6.25 (s, 1H, CH), 2.62 (br s, 3H, CH₃), 2.36 (br s, 3H, CH₃), –0.22 (br s, 3H, Al–CH₃), –0.45 (s, 3H, Al–CH₃), –1.73 (s, 3H, Al–CH₃), –1.82 (br s, 3H, Al–CH₃).
Synthesis of \((2-C_5H_4N)HC(3-CH_2C_8H_4N)(3-CH_2C_8H_4NH)Al(C(CH_3)_3)_2\) (6)

A solution of tri-tert-butylaluminum (0.282 g, 1.42 mmol) in 15 mL of toluene was added via cannula to a stirred suspension of 1 (0.500 g, 1.42 mmol) in toluene (15 mL). An immediate color change to orange was observed. The resulting solution was heated under reflux for 20 h. The solution was then reduced to 2-3 mL in vacuo and hexanes (20 mL) were added. A bright yellow precipitate was collected on a fine frit. Yield: 0.31 g, 45%.

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta 8.60 (d, ^3J_{HH} = 5.2 \text{ Hz}, 1\text{H, pyridyl H8}), 8.06 (t, ^3J_{HH} = 8.0 \text{ Hz}, 1\text{H, pyridyl H10}), 7.91 (d, ^3J_{HH} = 8.0 \text{ Hz}, 1\text{H, pyridyl H11}), 7.81 (d, ^3J_{HH} = 8.0 \text{ Hz}, 1\text{H, bound indolyl H7}), 7.79 (s, 1\text{H, NH}), 7.58 (t, ^3J_{HH} = 7.2 \text{ Hz}, 1\text{H, pyridyl H9}), 7.50 (d, ^3J_{HH} = 8.0 \text{ Hz}, 1\text{H, bound indolyl H4}), 7.46 (d, ^3J_{HH} = 8.0 \text{ Hz}, 1\text{H, free indole H7}), 7.18 (t, ^3J_{HH} = 8.0 \text{ Hz}, 1\text{H, bound indolyl H6}), 7.10 (d, ^3J_{HH} = 8.0 \text{ Hz}, 1\text{H, free indole H4}), 7.05 – 6.98 (m, 3\text{H, free indole H5, H6, bound indolyl H5 overlap}), 6.32 (s, 1\text{H, CH}), 2.57 (s, 3\text{H, CH}_3), 2.24 (s, 3\text{H, CH}_3), 1.32 (s, 9\text{H, C(CH}_3)_3), 0.52 (s, 9\text{H, C(CH}_3)_3). \(^{13}\)C\({^1}\)H NMR (CDCl\(_3\), 100.6 MHz): \(\delta 161.26 (s, \text{pyridyl-ipso}), 146.62 (s, \text{pyridyl C8}), 143.42 (s, \text{bound indolyl C3a}), 141.79 (s, \text{pyridyl C9}), 135.50 (s, \text{free indole C7a }), 135.17 (s, \text{bound indolyl C2}), 134.06 (s, \text{bound indolyl C7a}), 131.59 (s, \text{free indole C2}), 128.80 (s, \text{free indole C3a}), 127.96 (s, \text{pyridyl C10}), 122.62 (s, \text{pyridyl C11}), 122.08 (s, \text{free indole C6}), 120.04 (s, \text{bound indolyl C6}), 119.32 (s, \text{free indole C6}), 118.61 (s, \text{bound indolyl C6}), 118.49 (s, \text{free indole C7}), 117.86 (s, \text{bound indolyl C7}), 115.61 (s, \text{bound indolyl C4}), 110.94 (s, \text{free indole C4}), 110.73 (s, \text{bound indolyl C3}), 105.69 (s, \text{free indole C3}), 41.32 (s, \text{CH}), 32.26 (s, C(CH}_3)_3), 30.51 (s, C(CH}_3)_3), 16.72
Synthesis of (2-C₅H₄N)HC(3-CH₃C₈H₄N)(3-CH₃C₈H₄NH)Ga(C(CH₃)₃)₂ (7)

A solution of tri-tert-butylgallium (0.341 g, 1.42 mmol) in 15 mL of toluene was added via cannula to a stirred suspension of 1 (0.500 g, 1.42 mmol) in toluene (15 mL). The resulting solution was heated under reflux for 20 h. The solution was then reduced to 2-3 mL and hexanes (20 mL) were added. A bright yellow precipitate was collected on a fine frit. The solid was recrystallized by dissolving it in a minimum amount of hot toluene (2-3 mL) and adding hot hexanes (15 mL) until the solution becomes turbid. Hot toluene (0.5 mL) was added until turbidity disappears. The solution was cooled to 25 °C and stored at –30 °C overnight. A yellow crystalline solid was isolated by filtration through a fine frit. ¹H NMR (CDCl₃, 600 MHz): δ 8.44 (d, ³Jₜₜ = 5.4 Hz, 1H, pyridyl H8), 8.07 (br s, 1H, NH), 7.98 (t, ³Jₜₜ = 7.8 Hz, 1H, pyridyl H10), 7.87 (d, ³Jₜₜ = 7.8 Hz, 1H, pyridyl H11), 7.66 (d, ³Jₜₜ = 8.4 Hz, 1H, bound indolyl H7), 7.52 (d, ³Jₜₜ = 7.8 Hz, 1H, bound indolyl H4), 7.46 (dd, ³Jₜₜ = 5.4 Hz , ³Jₜₜ = 7.8 Hz, 1H pyridyl H9), 7.42 (d, ³Jₜₜ = 7.8 Hz, 1H, free indole H7), 7.14 (t, ³Jₜₜ = 7.8 Hz, 1H, bound indolyl H6), 7.06 (t, ³Jₜₜ = 7.2 Hz ,1H, bound indolyl H5), 7.02 – 6.97 (m, 3H, free indole H5, H6, H4 overlap), 6.23 (s, 1H, CH), 2.48 (s, 3H, CH₃), 2.29 (s, 3H, CH₃), 1.44 (s, 9H, C(CH₃)₃), 0.55 (s, 9H, C(CH₃)₃).¹³C{¹H} NMR (CDCl₃, 100.6 MHz): δ 160.93 (s, pyridyl- ipso), 147.63 (s, pyridyl C8), 144.03 (s, bound indolyl C3a), 140.88 (s, pyridyl C9), 136.06 (s, free indole C7a ), 135.20 (s, bound indolyl C2), 134.26 (s, bound indolyl C7a), 131.22 (s, free indole C2), 128.92 (s, free indole C3a), 127.76 (s, pyridyl C10), 122.47 (s, pyridyl...
C11), 121.80 (s, free indole C6), 119.64 (s, bound indolyl C6), 119.13 (s, free indole C6), 118.32 (s, bound indolyl C6), 117.98 (s, free indole C7), 117.90 (s, bound indolyl C7), 115.34 (s, bound indolyl C4), 110.89 (s, free indole C4), 109.89 (s, bound indolyl C3), 105.35 (s, free indole C3), 41.47 (s, CH), 32.18 (s, C(CH3)3), 30.39 (s, C(CH3)3), 24.95 (br s, C(CH3)3), 23.09 (br s, C(CH3)3), 9.42 (s, bound indolyl CH3), 9.03 (s, free indole CH3).

Synthesis of \((\text{2-C}_2\text{H}_4\text{N})\text{HC}(3-\text{CH}_3\text{C}_8\text{H}_4\text{N})_2\text{GaC(CH}_3)_3\) (8)

To a stirred solution of 1 (0.24 g, 0.68 mmol) in toluene (15 mL) an excess of two equivalents of tri-tert-butylgallium (0.340 g, 1.41 mmol) in 15 mL of toluene were added via cannula. An immediate color change to orange was observed. The resulting mixture was heated under reflux for 20 h. The solution volume was then reduced to 2-3 mL and hexanes (20 mL) were added. The solution was stored at –30 °C overnight. A bright yellow precipitate was collected on a medium frit. The \(^1\)H NMR spectrum of this solid indicated a mixture of 7 and 8 in approximate ratio 1:10. The solid was dissolved in hot toluene (10 mL) and kept at –30 °C overnight. An off-white solid precipitated and was collected on a fine frit. The \(^1\)H NMR spectrum of this solid indicated pure 8. Yield: 0.038 g, 10%. \(^1\)H NMR (CDCl₃, 600 MHz): δ 8.48 (d, \(^3\)Jₜₜ = 5.4 Hz, 1H, pyridyl H8), 7.84 (t, \(^3\)Jₜₜ = 7.8 Hz, 1H, pyridyl H10), 7.70 (d, \(^3\)Jₜₜ = 7.8 Hz, 1H, pyridyl H11), 7.45 (d, \(^3\)Jₜₜ = 7.2 Hz, 2H, indolyl H7), 7.44 (d, \(^3\)Jₜₜ = 7.2 Hz, 2H, indolyl H4), 7.28 (At, unresolved dd, 1H, pyridyl H9), 7.08 (t, \(^3\)Jₜₜ = 7.2 Hz, 2H, indolyl H5), 6.98 (t, \(^3\)Jₜₜ = 7.2 Hz, 2H, indolyl H6), 5.97 (s, 1H, CH), 2.46 (s, 6H, indolyl CH₃), 1.83 (s, 9H, Ga–C(CH₃)₃). \(^13\)C\{\(^1\)H\} NMR (CDCl₃, 150.8 MHz): δ 160.69 (s, pyridyl-ipso), 145.67 (s, pyridyl C8),
141.90 (s, pyridyl C9), 141.60 (s, C7a), 136.87 (s, C2), 130.30 (s, C3a), 125.00 (s, pyridyl C10), 122.60 (s, pyridyl C11), 120.65 (s, C5), 118.52 (s, C6), 117.95 (s, C7), 113.02 (s, C4), 106.81 (s, C3), 41.58 (s, CH), 29.91 (s, Ga−C(CH$_3$)$_3$), 21.52 (br s, Ga−C(CH$_3$)$_3$), 8.86 (s, indolyl-CH$_3$).

Synthesis of (2-C$_5$H$_4$N)HC(3-CH$_3$C$_8$H$_4$N)$_2$Al$_2$(C$_2$H$_5$)$_4$•C$_7$H$_8$ (9)

An excess of two equivalents triethylaluminum (0.400 g, 3.50 mmol) in 15 mL of toluene was added via cannula to a stirred solution of 1 (0.500 g, 1.42 mmol) in toluene (15 mL). An immediate color change to brownish yellow was observed. The resulting mixture was stirred at 20 °C for 2 h. The volume of the solution was reduced to 2-3 mL and then 25 mL of hexanes were added. The solution was stored at −30 °C overnight. The resulting bright yellow precipitate was collected on a medium frit. The solid was recrystallized by dissolving in a minimum amount of hot toluene (2 mL), adding 20 mL of hot hexanes and storing the solution at −30 °C overnight. A yellow precipitate was collected on a medium frit and dried under vacuum for 5 h. Yield: 0.50 g, 58%. $^1$H NMR (CDCl$_3$, 600 MHz): δ 8.31 (d, $^3$J$_{HH}$ = 6.0 Hz, 1H, pyridyl H8), 7.98 (t, $^3$J$_{HH}$ = 8.4 Hz, 1H, pyridyl H10), 7.87 (d, $^3$J$_{HH}$ = 8.4 Hz, 1H, pyridyl H11), 7.83 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H, bridging indolyl H7), 7.56 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H, bound indolyl H7), 7.49–7.38 (m, 5H, bound indolyl H4, bridging indolyl H5, bound indolyl H6, bridging indolyl H6, pyridyl H9, overlap), 7.02-6.97 (m, 2H, bridging indolyl H4, bound indolyl H5, overlap), 6.22 (s, 1H, CH), 2.64 (s, 3H, indolyl CH$_3$), 2.35 (s, 3H, indolyl CH$_3$), 1.17 (t, $^3$J$_{HH}$ = 8.4 Hz, 3H, CH$_2$CH$_3$), 0.97 (t, $^3$J$_{HH}$ = 8.4 Hz, 3H, CH$_2$CH$_3$), 0.66 (m, 1H, CH$_2$CH$_3$), 0.46 (m, 1H, CH$_2$CH$_3$), 0.32 (m, 1H, CH$_2$CH$_3$), 0.11 (t, $^3$J$_{HH}$ = 8.4 Hz, 3H, CH$_2$CH$_3$), 0.04 (m, 1H,
$^{13}$C{${}^1$H} NMR (CDCl$_3$, 150.8 MHz): $\delta$ 161.57 (s, pyridyl-ipso), 144.87 (s, bound indolyl C3a), 144.26 (s, pyridyl C8), 143.20 (s, bridging indolyl C7a), 142.04 (s, pyridyl C9), 139.78 (s, bridging indolyl C2), 136.98 (s, bridging indolyl C3a), 136.61 (s, bound indolyl C2), 131.13 (s, indolyl bound C7a), 127.91 (s, pyridyl C10), 124.62 (s, bridging indolyl C6), 124.32 (s, bound indolyl C6), 123.60 (s, bridging indolyl C3), 123.46 (s, pyridyl C11), 120.42 (s, bridging indolyl C4), 119.83 (s, bound indolyl C7), 117.91 (s, bound indolyl C5), 117.83 (s, bound indolyl C4), 117.48 (s, bridging indolyl C7), 113.98 (s, bridging indolyl C5), 105.60 (s, bridging indolyl C3), 41.16 (s, CH), 10.25 (s, CH$_2$CH$_3$), 9.94 (s, CH$_2$CH$_3$), 9.52 (s, bound indolyl CH$_3$), 9.38 (s, CH$_2$CH$_3$), 8.37 (s, CH$_2$CH$_3$), 7.96 (s, bridging indolyl CH$_3$), 2.57 (br s, CH$_2$CH$_3$), 1.04 (br s, CH$_2$CH$_3$), –1.30 (br s, CH$_2$CH$_3$), –3.28 (br s, CH$_2$CH$_3$). Anal. Calcd for C$_{32}$H$_{39}$N$_3$Al$_2$: C, 73.96; H, 7.56; N, 8.08. Found: C, 71.93; H, 8.04; N, 7.73.

**X-ray Crystallography**

Crystals of 6 were obtained from toluene by slowly cooling the reaction filtrate to –30 °C. Crystals of 3 were similarly obtained from toluene by slowly cooling the reaction mixture to –30 °C. X-ray diffraction data were collected on a Siemens three-circle platform diffractometer equipped with a 2K CCD detector. The frame data were acquired with the SMART 5.625$^9$ software using Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Cell constants were determined with SAINT 6.22$^{10}$ from the complete dataset. A complete sphere was scanned on $\omega$ (0.3°) with run time of 60 s/frame for 6. A total of 1600 frames were collected for the dataset. An additional 50 frames, identical to the first 50 frames, were
collected to determine crystal decay. For 3, a complete sphere scan was initiated on \( \omega \) (0.3\(^\circ\)) with run time of 45 s/frame. Data acquisition was aborted 44 frames into the fourth run due to technical problems. A total of 1691 frames were collected for the dataset. The frames were integrated using the SAINT 6.22 software and the data were corrected for absorption and decay using the SADAB\(^{11}\) program. The structures were solved by direct methods using SHELXS 6.10\(^{12}\) and refined by least-squares methods on \( F^2 \), using SHELXL 6.10.\(^{13}\) Details of data collection and refinement and unit cell parameters for 3 and 6 are provided in Table 2.1.
Table 2.1. Summary of X-ray Crystallographic Data

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>6</th>
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<tbody>
<tr>
<td>formula</td>
<td>C$<em>{35}$H$</em>{39}$N$<em>{3}$Al$</em>{2}$</td>
<td>C$<em>{32}$H$</em>{38}$N$_{3}$Al</td>
</tr>
<tr>
<td>fw</td>
<td>555.65</td>
<td>491.63</td>
</tr>
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<td>crystal system</td>
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<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
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<td>C$_{2}$/c</td>
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<td>a, Å</td>
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<td>20.071(5)</td>
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<tr>
<td>b, Å</td>
<td>12.6427(16)</td>
<td>15.032(4)</td>
</tr>
<tr>
<td>c, Å</td>
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<td>18.695(4)</td>
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<td>a, deg</td>
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<td>90</td>
</tr>
<tr>
<td>β, deg</td>
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<td>100.562(7)</td>
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<tr>
<td>γ, deg</td>
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<td>90</td>
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<td>V, Å$^3$</td>
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<td>5545(2)</td>
</tr>
<tr>
<td>Z</td>
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<td>8</td>
</tr>
<tr>
<td>Dcalcd, g cm$^{-3}$</td>
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<td>1.178</td>
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<td>T, °C</td>
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<td>–123</td>
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<tr>
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<tr>
<td>λ, Å</td>
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<td>0.710 73</td>
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<td>1.00-0.845</td>
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<td>2θ limits, deg</td>
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<td>21627</td>
</tr>
<tr>
<td>no. of unique data</td>
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<td>4878</td>
</tr>
<tr>
<td>no. of obsd data$^a$</td>
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<td>4016</td>
</tr>
<tr>
<td>no. of params</td>
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<td>325</td>
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<td>R1$^b$</td>
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<td>0.0659</td>
</tr>
<tr>
<td>wR2$^c$</td>
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<td>0.1271</td>
</tr>
<tr>
<td>max, min peaks, e/Å$^3$</td>
<td>0.277, – 0.277</td>
<td>0.370, – 0.257</td>
</tr>
</tbody>
</table>

$^a$ I > 2σ(I).  $^b$ R1 = Σ ||F$_o$| – |F$_c$| | / Σ |F$_o$|.  $^c$ wR2 = [Σ[w (F$_o^2$ – F$_c^2$)$^2$] / Σ[w (F$_o^2$)$^2$]]$^{1/2}$.  

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2.3 Results and discussion

2.3.1 Modified preparation of 1

Fneich synthesized di(3-methylindolyl)pyridylmethane (1) by reaction of 3-methylindole with pyridine carbaldehyde, followed by deprotonation using Amberlite IRA–67 ion exchange resin (eqs 2 and 3). During deprotonation (eq 3), Fneich observed that the protonated ligand was only sparingly soluble in hot acetonitrile. This resulted in the use of excess hot acetonitrile to dissolve the protonated ligand. While attempting to repeat the preparation, it was observed that though the protonated ligand is insoluble in acetonitrile, after deprotonation, the neutral ligand is soluble in acetonitrile. This observation allowed us to initiate the reaction with a suspension of [1•H]⁺ in acetonitrile at room temperature and as the deprotonation proceeded, 1 dissolved in the solvent. By
adopting the above modification we were able to reduce solvent consumption by almost six-fold from the initial reported synthesis.

Fneich also used excess Amberlite IRA–67 ion exchange resin in the deprotonation step. The resin has an ion exchange capability of 1.6 mg/meq, thus in the modified preparation it was stoichiometrically added. This resulted in the use of less resin consumption than previously reported.

### 2.3.2 Synthesis of bidentate complexes of 1 with \(^{t}Bu_{3}Al\) and \(^{t}Bu_{3}Ga\)

To investigate the reasons for low yields for 2d, the reaction of 1 with tri-tert-butylaluminum was repeated. Unexpectedly, the reaction yielded the previously unobserved bidentate complex 6 in 45% yield (eq 4).

![Reaction Scheme](image)

The \(^1\)H NMR spectrum of 6 in benzene-\(d_6\) has two singlet resonances at 1.32 ppm and 0.51 ppm each integrating to nine protons. These are assigned to the two chemically inequivalent tert-butyl groups on the aluminum. There are two singlets at 2.56 ppm and 2.24 ppm, each corresponding to a chemically inequivalent methyl group on the two indoles. In the aromatic region of the spectrum there are two distinct sets of resonances.
for the protons on the two chemically inequivalent indoles. A broad resonance at 7.78 ppm integrating to one proton indicates that one of the indole ring is still protonated. A singlet methine resonance at 6.31 ppm indicates that there is one species as the product as opposed to a mixture. The resonance corresponding to H7 on one of the indoles is shifted downfield. This is consistent with the observation made by Mason\textsuperscript{7} and co-workers that phosphine derivatives of indolyl ligands result in the indolyl H7 resonance being shifted downfield. The $^{13}$C NMR spectrum similarly has two broad resonances at 16.72 ppm and 15.31 ppm corresponding to the two quaternary carbons for the tert-butyl groups bound to aluminum. There are also distinct resonances at 32.26 ppm and 30.51 ppm corresponding to the two nonequivalent methyl groups on the tert-butyl groups as well as two distinct resonances at 9.52 ppm and 8.88 ppm arising from the two chemically inequivalent methyl groups on the two indoles. There is one resonance at 41.32 ppm corresponding to the methine carbon. There are two distinct sets of resonances in the aromatic region for the carbons on the two indoles. One set of resonances in this region has chemical shifts very close to the corresponding resonances in the free ligand 1. We have assumed that this set of resonances arises due to the carbons on the free indole arm. The chemical shifts of the other set of resonances shows substantial resemblance to the set of aromatic carbon resonances observed for 2d, thus substantiating our assumption that these arise from the carbons in the bound indolyl ring.

X-ray quality crystals of 6 were obtained by slowly cooling the reaction filtrate to $-30$ $^\circ$C. A suitable crystal was mounted on the diffractometer and the structure was elucidated from the data collected. The molecular structure of 6 is shown in Figure 2.4. A selection of bond distances and angles is shown in Table 2.2. The crystal structure
confirms the structure proposed on the basis of NMR spectral data. One of the indolyl arms of 1 is deprotonated and coordinated to aluminum while the other indolyl arm is free. The pyridyl nitrogen is also coordinated to the aluminum to form a six-membered chelate ring. The aluminum is approximately tetrahedral with angles in the range 95.06(10)° to 121.63(12)°. The Al–N\textsubscript{indolyl} distance is 1.884(2) Å. This is comparable to the Al–N\textsubscript{indolyl} distances of 1.845(6) Å and 1.870(6) Å reported by Fneich\textsuperscript{2} for 2b. This distance is also comparable to the average Al–N\textsubscript{pyrrolyl} distances of 1.825 Å reported for (pyrrolyl)\textsubscript{3}Al•(Me\textsubscript{2}NH) by Cowley\textsuperscript{14} and co-workers. In the complex (3-methylindolyl)\textsubscript{3}Al•NHMe\textsubscript{2} the average Al–N\textsubscript{indolyl} distance is 1.863 Å.\textsuperscript{15}

**Figure 2.4.** ORTEP diagram of 6. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, except the indole NH, are omitted for clarity.
Table 2.2. Selected bond distances and angles for 6

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
<th>Bond angles (deg)</th>
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<tbody>
<tr>
<td>N1–Al 1.884(2)</td>
<td>C1–C11 1.504(4)</td>
</tr>
<tr>
<td>N3–Al 2.009(2)</td>
<td>C11–N1 1.399(3)</td>
</tr>
<tr>
<td>N3–C2 1.351(2)</td>
<td>C1–C21 1.509(4)</td>
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<tr>
<td>N1–Al–N3 95.06(10)</td>
<td>C28–N2–C21 109.1(2)</td>
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<td>N3–Al–C31 101.41(11)</td>
<td>C2–N3–C6 118.2(2)</td>
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<tr>
<td>N1–Al–C31 109.20(11)</td>
<td>C2–N3–Al 124.54(17)</td>
</tr>
<tr>
<td>N3–Al–C41 110.72(11)</td>
<td>C6–N3–Al 113.58(19)</td>
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<tr>
<td>N1–Al–C41 114.69(11)</td>
<td>N2–C21–C1 118.8(2)</td>
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<tr>
<td>C41–Al–C31 109.20(11)</td>
<td>N3–C2–C1 119.3(2)</td>
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<tr>
<td>C11–N1–Al 127.18(17)</td>
<td>C2–C1–C11 117.2(2)</td>
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<tr>
<td>C18–N1–C11 104.7(2)</td>
<td>C1–C11–N1 120.7(2)</td>
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<td>C18–N1–Al 126.81(18)</td>
<td></td>
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</tbody>
</table>

The Al–N<sub>pyridyl</sub> distance is 2.009(2) Å. The corresponding bond length in 2b is 1.980(5) Å and as discussed by Fneich,<sup>2</sup> we may designate it as a Al–N dative bond. The interior angles in the six-membered C11–N1–Al–N3–C2–C1 ring lie in the range of 117.2(2)<sup>°</sup> to 127.18(17)<sup>°</sup> and are all close to 120° except the angle N1–Al–N3 that is 95.06(10)<sup>°</sup>. Thus we can say that the aluminum fits into quite well the “cavity” made by the ligand nitrogens.

Now we discuss the angles around the nitrogen atoms. The discussion of this is significant since if the sum of the three angles around nitrogen is 360° then it is planar with the other three atoms surrounding it. The sum of the angles around N1 and N3 are
358.69° and 356.32°, respectively, indicating that they are essentially planar, as expected, for aromatic indole and pyridine rings.

The analogous gallium complex, 7, was synthesized by a procedure analogous to the preparation of 6 (eq 4). The $^1$H and $^{13}$C NMR spectroscopic data for 7 is similar to that of 6. The reaction filtrate yielded X-ray quality crystals of 7. After collection of X-ray data, attempts to solve the crystal structure revealed the crystal to be twinned.

On reacting one equivalent of triethylaluminum with 1, pure 2b was obtained at 20 °C after 1.5 h stirring. Thus the bulk of the alkyl groups on aluminum might play a role in the reaction mechanism. We may also propose that the reaction might proceed through the bidentate intermediate and for tri-tert-butylaluminum the conversion from the bidentate complex to the tridentate complex may be energetically unfavorable. Further studies are necessary to elucidate the mechanism of the reaction. It might be noted that an excess of one equivalent of tri-tert-butylgallium or tri-tert-butylaluminum results in a mixture of 7 and 8 for the former and 2d and 6 for the latter.

### 2.3.3 Synthesis and characterization of the bimetallic complexes 3 and 9.

Compound 3 was prepared by reaction of 1 with two equivalents of Me$_3$Al using the modified version (eq 5) of the procedure reported by Fneich. The NMR spectroscopic data matched that previously reported for 3. X-ray quality crystals were obtained by slowly cooling the reaction mixture to –30 °C.
The molecular structure of 3 is provided in Figure 2.5 and selected bond distances and angles are provided in Table 2.3. There are two aluminum atoms bridged by an indolyl moiety as opposed to a methyl group as proposed earlier. A terminal indolyl and a terminal pyridyl moiety are attached to the two aluminums, respectively. The distances between the nitrogen on the bridging indolyl and the two aluminums are 2.022(2) Å and 1.969(2) Å respectively.

Figure 2.5. ORTEP diagram of 3. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.
Table 2.3. Selected bond distances and angles for 3

<table>
<thead>
<tr>
<th>Bond distances (Å)</th>
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<tbody>
<tr>
<td>N1–Al1 1.885(2)</td>
<td>Al2–N2 1.969(2)</td>
</tr>
<tr>
<td>Al1–N2 2.022(2)</td>
<td>Al2–N3 1.968(2)</td>
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</table>

<table>
<thead>
<tr>
<th>Bond angles (deg)</th>
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<tr>
<td>N2–Al1–N1 98.78(9)</td>
<td>C2–C1–C21 116.4(2)</td>
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<tr>
<td>N3–Al2–N2 93.70(9)</td>
<td>C2–C1–C11 109.37(19)</td>
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<tr>
<td>Al2–N2–Al1 123.35(10)</td>
<td>C21–C1–C11 110.87(19)</td>
</tr>
<tr>
<td>Al2–N3–C6 115.20(18)</td>
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</tr>
</tbody>
</table>

In the literature indolyl bridging complexes are known. Weiss\textsuperscript{16} and coworkers synthesized dimeric lithium and sodium complexes with bridging indolyl groups. The M–N\textsubscript{bridging indolyl} bond distances are 2.331 Å and 2.004 Å for M = Li and lie in the range of 2.356 to 2.478 Å for M = Na. The average bond length for indolyl bridge disodium complexes synthesized by Dehnicke\textsuperscript{17}\textsuperscript{18} and co-workers is 2.448 Å. In the Mason group\textsuperscript{18} complexes of aluminum alkyls with di- and tri(3-methylindolyl) methanes with N–indolyl bridges have recently been synthesized and characterized. The average Al–N\textsubscript{indolyl bridge} bond distance for these complexes are 2.044 Å, 1.99 Å and 2.00 Å. This is comparable to the corresponding bond distance in 3. Other examples of structures with indolyl moieties bridging main group metals are provided in chapter 1.

The ethyl analog of 3, complex 9, was prepared by a procedure analogous to the preparation of 3 (eq 5). The aromatic region of the \textsuperscript{1}H NMR spectrum of 9 in chloroform-
$d$ is not well resolved in the region 7.5 ppm to 6.5 ppm, where most of the indolyl resonances show up. The pyridyl H8, H9 and H11 appear much downfield and they are clearly distinguishable as a doublet, triplet and a doublet at 8.31 ppm, 7.98 ppm and 7.87 ppm, respectively. Previous studies on di(3-methylindolyl)methanes by Mason and co-workers have indicated that the indolyl H7 resonance shifts downfield on complexation, therefore we can tentatively assign the doublet at 7.83 ppm to H7 in the bound indolyl. By comparison of assignments in the di(3-methylindolyl)imidazolylmethane complexes to be described in chapter 3, we may assign the doublet at 7.56 ppm to be the H4 on the bound indolyl. There is a multiplet from 7.49 to 7.37 ppm which contains aromatics including toluene. This multiplet integrates to five hydrogens. There is a single methine resonance at 6.22 ppm.

In the aliphatic region, there are two resonances at 2.64 ppm and 2.35 ppm (the toluene methyl resonance is buried in this) corresponding to the methyls on the two nonequivalent indolyls. There are four ethyl groups, two each on each of the two aluminums. The four methyls on these four ethyls appear as four triplets each integrating to 3H at 1.70 ppm, 0.97 ppm, 0.12 ppm and 0.11 ppm. The eight methylene protons on these four ethyls are all diastereotopic and they appear as eight distinct multiplets at 0.66 ppm, 0.46 ppm, 0.32 ppm, 0.04 ppm, –0.77 ppm, –0.92 ppm, –0.99 ppm and –1.22 ppm each integrating to one hydrogen. The splitting pattern of the methylene protons corresponds to the AB portion of an ABX$_3$ system. The $^{13}$C NMR spectroscopic data confirms our interpretation of the $^1$H NMR spectroscopic data. There are four resonances at 10.25 ppm, 9.94 ppm, 9.38 ppm and 8.37 ppm for the methyl carbons and four upfield shifted resonances at 2.57 ppm, 1.04 ppm, –1.30 ppm and –3.28 ppm for the methylene carbons.
on the ethyl substituents on aluminum. There are two sets of resonances for the two chemically inequivalent indolyl moieties. A noteworthy feature of 3 and 9 is that their solutions in toluene, chloroform-$d$ and benzene-$d_6$ are fluorescent (greenish yellow).

2.4 Conclusions

Two bidentate complexes of di(3-methylindolyl)pyridylmethane (1), HLM$^\text{Bu}_2$ (LH$_2$ = 1; M = Al (6), Ga (7)) have been synthesized. Two bimetallic complexes LAl$_2$R$_4$ (LH$_2$ = 1; R = Me (3), Et (9)) have also been synthesized. All complexes were characterized by $^1$H and $^{13}$C NMR spectroscopy. Complexes 3 and 6 were characterized X-ray crystallographically. The crystal structure of 3 shows that the two aluminum atoms are bridged by an indolyl group. This is the first known example of a group 13 complex to contain a bridging N-indolyl group.

2.5 References

(2) Fneich, B. N. Ph.D. Dissertation, University of Toledo, Toledo, Ohio, August 2006.


(18) Kingsley, N. B.; Mason, M. R., unpublished result.
Chapter Three

Synthesis and Characterization of Di(3-methylindolyl)imidazolylmethane Complexes of Aluminum and Gallium

3.1 Introduction

Di(3-methylindolyl)methanes are being investigated as ligands for complexation with various main group (Al, B, Si) and transition (Ti, Zr, Hf) elements. The property that makes diindolylmethanes different from the amido, pyrazolyl and imidazole ligands is their strong electron-withdrawing ability when bound in a $\eta^1$ mode. This was also assumed to cause a reduced tendency for $\pi$-donation and M–N–M bridging thus resulting in monometallic complexes. This is because the lone pair on the indole nitrogen is delocalized in the aromatic framework. It may be noted here that, as discussed later, only a few bimetallic complexes of main group elements with a bridging N-indolyl moiety are reported in literature. Previously in the Mason group a series of di(3-methylindolyl)methane ligands have been synthesized by acid-catalyzed condensation of 3-methylindole with the corresponding aldehyde. Subsequently, several metal complexes of these ligands have been synthesized and characterized.

The steric and electronic properties of this class of ligands can be fine-tuned by varying the substituents on the ligand backbone. A diverse library of ligands with
different substituents is therefore useful to probe complexation behavior. Fneich\(^1\) synthesized di(3-methylindolyl)pyridylmethane, and on reaction with aluminum alkyls generated tridentate neutral monoalkyl complexes as discussed in chapter 2. Subsequent attempts of alkyl abstraction to generate a three-coordinate cationic aluminum complex led to unidentified products. Such cationic complexes are highly Lewis acidic in nature and are thus potential catalysts\(^6\) for various processes like ethylene polymerization and binding and activating carbon monoxide\(^7\).

To probe the reactivity of such complexes further, a new ligand of this class, di(3-methylindolyl)-N-methylimidazolylmethane (1) has been synthesized. The fundamental difference of this ligand from its pyridyl analog is the difference in basicity of the pyridyl and the N-methylimidazolyl substituents. The pKa value for the protonated pyridyl group is 5.20 while that for the protonated N-methylimidazolyl is 6.95. Thus the imidazolyl nitrogen is more basic than the pyridyl nitrogen, and likely to coordinate more strongly to the central metal. There are examples of adducts of N-methylimidazole with boron,\(^8\) aluminum,\(^9\) and gallium.\(^10\) The similarities of 1 with its pyridyl analog include similar structure and chelate sizes. Both ligands have a backbone of two indole rings and a neutral donor nitrogen from a third moiety, in one case pyridyl and in the other case N-methylimidazolyl.

\[ \text{Diagram of ligand 1} \]
Herein we report the synthesis and characterization of di(3-methylindolyl)-N-
methylimidazolymethane (1). We also report the synthesis of bidentate dialkyl aluminum complexes 2a-d as well as a gallium analog 3. The synthesis and characterization of the bimetallic complexes 4a and 4b is also described.

<table>
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<th>Complex</th>
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<tr>
<td>2a</td>
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<td>2b</td>
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<td>2d</td>
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<tr>
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<td>Ga</td>
<td>'Bu</td>
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3.2 Experimental Section

**General Procedures.** All reactions involving aluminum and gallium alkyls were performed under an atmosphere of purified nitrogen using standard inert atmosphere techniques. Hexanes and acetonitrile were distilled from calcium hydride prior to use. Toluene was distilled from sodium. Chloroform-\textit{d} and benzene-\textit{d}_6 were dried by storage over activated 4Å molecular sieves. Trimethylaluminum (2.0 M in toluene), triethylaluminum (neat), tri-\textit{iso}-butylaluminum (neat), 3-methylindole, N-methylimidazole, Amberlite IRA-67 and anhydrous aluminum chloride were purchased
from Aldrich Chemical. Tri-tert-butylaluminum was prepared by modification of the procedure reported by Lehmkul\textsuperscript{11} and Uhl.\textsuperscript{12} Tri-tert-butylgallium was prepared as reported by Kovar\textsuperscript{13} and coworkers. 1-Methyl-2-formylimidazole was prepared by the procedure of Oberhausen\textsuperscript{14} and coworkers.

Solution NMR spectra were recorded on a Varian Unity 400 or Varian Inova 600 spectrometer. Chemical shifts are reported relative to tetramethylsilane. Two-dimensional NMR spectra were recorded on a Varian Inova 600 spectrometer. The $^{13}$C NMR spectra assignments are based on HMBC and HMQC experiments. Some of the $^{13}$C NMR spectra assignments are tentative and based on previously reported NMR assignments for diindolylmethanes\textsuperscript{1,5} as well as on NMR assignments of indole derivatives reported by Park.\textsuperscript{15} The numbering scheme for the imidazole and indole rings of compound 1 is shown in Figure 3.1.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. High-resolution mass spectrometric analysis (TOF ES) was provided by the Mass Spectrometry and Proteomics Facility at The Ohio State University.

![Figure 3.1. Numbering scheme for ligand 1](image)

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Synthesis of [(1-CH₃-2-C₃H₂N₂H)HC(3-CH₃C₈H₄NH)$_₂$][HSO₄] (1·H)[HSO₄])

This procedure is based on that previously developed by Dr. Mark Mason and undergraduate researcher Laura Seig. N-Methylimidazole-2-carbaldehyde (6.16 g, 0.0555 mol) was added to a stirred solution of 3-methylindole (14.7 g, 0.112 mol) in 30 mL of absolute ethanol. Concentrated H₂SO₄ (5 mL) was added to the solution. The solution turned yellow and was refluxed for 1.5 h to form a yellow precipitate which was collected on a medium frit, washed with cold ethanol (2 × 5 mL) and dried by air flow. This resulted in a white powdery solid. Yield: 11 g, 42%. $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 10.84 (br s, 2H, NH), 7.74 (br s, 1H, imidazolyl H₄), 7.55 (br s, 1H, imidazolyl H₅), 7.49 (d, $^3$J$_{HH}$ = 7.6 Hz, 2H, indolyl H₇), 7.33 (d, $^3$J$_{HH}$ = 7.6 Hz, 2H, indolyl H₄), 7.09 (t, $^3$J$_{HH}$ = 7.6 Hz, 2H, indolyl H₆), 7.01 (t, $^3$J$_{HH}$ = 7.6 Hz, 2H, indolyl H₅), 6.60 (br s, 1H, CH), 3.50 (s, 3H, imidazolyl CH₃), 2.11 (s, 6H, indolyl-CH₃).

Synthesis of (1-CH₃-2-C₃H₂N₂)HC(3-CH₃C₈H₄NH)$_₂$ (1)

Amberlite IRA-67 (50 mL, 80 meq.) was added to a stirred suspension of [1·H][HSO₄] (10.6 g, 0.0235 mol) in 120 mL of acetonitrile and the mixture was stirred at 25 °C under nitrogen flow for 1 h resulting in a clear light green solution. The Amberlite was filtered off and solvent was removed from the filtrate in vacuo resulting in a powdery, yellow solid 1. Yield: 8.0 g, 96%. $^1$H NMR (CDCl₃, 600 MHz): δ 9.41 (br s, 2H, NH), 7.47 (d, $^3$J$_{HH}$ = 7.8 Hz, 2H, indolyl H₇), 7.28 (d, $^3$J$_{HH}$ = 7.8 Hz, 2H, indolyl H₄), 7.10 (t, $^3$J$_{HH}$ = 7.8 Hz, 2H, indolyl H₅), 7.09 (d, $^3$J$_{HH}$ = 1.2 Hz, 1H, imidazolyl H₄), 7.07 (t, $^3$J$_{HH}$ = 7.8 Hz, 2H, indolyl H₆), 6.77 (d, $^3$J$_{HH}$ = 1.2 Hz, 1H, imidazolyl H₅), 5.94 (s, 1H, CH), 3.69 (s, 3H, imidazolyl CH₃), 2.39 (s, 6H, indolyl CH₃). $^{13}$C{$^1$H} NMR
(CDCl$_3$, 150.8 MHz): $\delta$ 146.36 (s, imidazolyl C2), 135.41 (s, indolyl C7a), 131.48 (s, indolyl C2), 128.64 (s, indolyl C3a), 127.22 (s, imidazolyl C4), 121.62 (s, indolyl C5), 120.75 (s, imidazolyl C5), 118.99 (s, indolyl C6), 118.31 (s, indolyl C7), 110.97 (s, indolyl C4), 106.56 (s, indolyl C3), 32.67 (s, 1H, CH), 30.97 (s, imidazolyl CH$_3$), 8.78 (s, indolyl CH$_3$).

$^1$H NMR (C$_6$D$_6$, 400 MHz): $\delta$ 9.73 (br s, 2H, NH), 7.59 (d, $^3$J$_{HH}$ = 7.6 Hz, 2H, indolyl H7), 7.21-7.10 (m, aromatics), 7.05 (s, 1H, imidazolyl H4), 6.98 (d, $^3$J$_{HH}$ = 8.4 Hz, 2H, indolyl H4) 6.06 (s, 1H, imidazolyl H5), 5.58 (s, 1H, CH), 2.49 (s, 3H, imidazolyl CH$_3$), 2.27 (s, 6H, indolyl CH$_3$).

$^1$H NMR (DMSO-$d_6$, 600 MHz): $\delta$ 10.82 (br s, 2H, NH), 7.47 (d, $^3$J$_{HH}$ = 7.8 Hz, 2H, indolyl H7), 7.40 (d, $^3$J$_{HH}$ = 7.8 Hz, 2H, indolyl H4), 7.12 (s, 1H, imidazolyl H4), 7.09 (t, $^3$J$_{HH}$ = 7.8 Hz, 2H, indolyl H5), 7.08 (t, $^3$J$_{HH}$ = 7.8 Hz, 2H, indolyl H6), 6.98 (s, 1H, imidazolyl H5), 6.17 (s, 1H, CH), 3.61 (s, 3H, imidazolyl CH$_3$), 2.34 (s, 6H, indolyl CH$_3$). $^{13}$C($^1$H) NMR (DMSO-$d_6$, 150.8 MHz): $\delta$ 145.85 (s, imidazolyl C2), 135.49 (s, indolyl C7a), 132.47 (s, indolyl C2), 128.24 (s, indolyl C3a), 126.20 (s, imidazolyl C4), 121.82 (s, indolyl C5), 120.91 (s, imidazolyl C5), 118.32 (s, indolyl C6), 118.07 (s, indolyl C7), 111.09 (s, indolyl C4), 105.85 (s, indolyl C3), 32.47 (s, imidazolyl CH$_3$), 32.06 (s, CH), 8.41 (s, indolyl CH$_3$). HRMS (ES) m/z for C$_{23}$H$_{23}$N$_4$ (M+H$^+$): calcd, 355.1922; found 355.1922. Anal. Calcd for C$_{23}$H$_{23}$N$_4$: C, 77.94; H, 6.26; N, 15.81. Found: C, 77.99; H, 5.99; N, 15.88.
Synthesis of (1-CH$_3$-2-C$_3$H$_2$N$_2$)HC(3-CH$_3$C$_8$H$_4$NH)(3-CH$_3$C$_8$H$_4$N)Al(CH$_3$)$_2$ (2a)

Exactly one equivalent of trimethylaluminum (1.0 mL, 2.0 mmol, 2.0 M solution in toluene) was added via syringe to a suspension of 1 (0.708 g, 2.00 mmol) in freshly distilled toluene (20 mL). A clear yellow solution resulted immediately. The solution was stirred at 25 °C for 2 h during which the color of the solution changed to dark blue. Thereafter, it was stored at −30 °C overnight. A white needle-like crystalline solid was isolated by filtration through a fine Schlenk frit. The solid was recrystallized from hot toluene (10 mL) yielding 2a as a toluene solvate (~ 0.63 C$_7$H$_8$). Yield: 0.75 g, 77%. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.91 (br s, 1H, NH), 7.56 (d, $^3$J$_{HH}$ = 7.6 Hz, 1H, bound indolyl H7), 7.44 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H, free indole H7), 7.43 (d, 1H, bound indolyl H4), 7.11-7.09 (m, 1H, bound indolyl H6), 7.03-7.00 (m, 4H, bound indolyl H5, free indole H6, free indole H5, free indole H4 overlap), 6.93 (d, $^3$J$_{HH}$ = 1.6 Hz, 1H, imidazolyl H4), 6.56 (d, $^3$J$_{HH}$ = 1.6 Hz, 1H, imidazolyl H5), 5.91 (s, 1H, CH), 3.47 (s, 3H, imidazolyl CH$_3$), 2.41 (s, 3H, bound indolyl CH$_3$), 2.28 (s, 3H, free indole CH$_3$), −0.39 (s, 3H, Al–CH$_3$), −0.52 (s, 3H, Al–CH$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$, 100.6 MHz): $\delta$ 148.15 (s, imidazolyl C2), 142.52 (s, bound indolyl C3a), 135.82 (s, free indole C7a), 134.50 (s, bound indolyl C2), 130.62 (s, bound indolyl C7a), 129.96 (s, free indole C2), 128.19 (s, free indole C3a), 123.43 (s, free imidazolyl C4), 122.49 (s, free indole C6), 122.45 (s, imidazolyl C5), 120.25 (s, bound indolyl C6), 119.41 (s, free indole C5), 118.58 (s, bound indolyl C5), 118.11 (s, free indole C7), 117.92 (s, bound indolyl C4), 113.58 (s, bound indolyl C7), 110.72 (s, free indole C4), 108.37 (s, bound indolyl C3), 105.93 (s, free indole C3), 33.64 (s, imidazolyl CH$_3$), 32.25 (s, CH), 9.31 (s, bound indolyl CH$_3$), 8.97 (s, free indole CH$_3$), −8.21 (br s, Al–CH$_3$), −9.88 (br s, Al–CH$_3$).
\(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz): \(\delta\) 8.04 (br s, 1H, NH), 8.01 (d, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, bound indolyl H7), 7.77 (d, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, bound indolyl H4), 7.49 (d, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, free indole H7), 7.40 (t, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, bound indolyl H6), 7.34 (t, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, bound indolyl H5), 7.11 (t, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, free indole H6), 6.98 (t, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, free indole H4), 6.39 (d, \(^3\)J\(_{HH}\) = 1.2 Hz, 1H, imidazolyl H4), 5.40 (d, \(^3\)J\(_{HH}\) = 1.2 Hz, 1H, imidazolyl H5), 5.38 (s, 1H, CH), 2.33 (s, 3H, imidazolyl CH\(_3\)), 2.18 (s, 3H, bound indolyl CH\(_3\)), 2.13 (s, 3H, free indole CH\(_3\)), 0.04 (s, 3H, Al–CH\(_3\)), –0.01 (s, 3H, Al–CH\(_3\)).

**Synthesis of \((1-\text{CH}_3-2-\text{C}_3\text{H}_2\text{N}_2)\text{HC}(3-\text{CH}_3\text{C}_8\text{H}_4\text{NH})(3-\text{CH}_3\text{C}_8\text{H}_4\text{N})\text{Al}(\text{C}_2\text{H}_5)_2\) (2b)**

A solution of triethylaluminum (0.161 g, 1.41 mmol) in 10 mL of toluene was added via cannula to a suspension of 1 (0.500 g, 1.41 mmol) in freshly distilled toluene (30 mL). A clear yellow solution resulted immediately. The solution was stirred at 25 °C for 2 h and stored at –30 °C. A yellow precipitate was observed after 4 h. The solution was concentrated to about 20 mL and stored at –30 °C overnight. The resulting yellow solid was isolated by filtration through a fine Schlenk frit (yield: 0.250 g). The filtrate was concentrated to half the original volume and kept at –30 °C overnight. A second crop was isolated by filtration through a fine Schlenk frit (yield: 0.050 g). The two crops were combined and recrystallized from hot toluene (10 mL) to yield 2b as a toluene solvate (~0.25 C\(_7\)H\(_8\)). Yield: 0.21 g, 33%. \(^1\)H NMR (C\(_6\)D\(_6\), 600 MHz): \(\delta\) 8.00 (d, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, bound indolyl H7), 7.99 (br s, 1H, NH), 7.71 (d, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, bound indolyl H4), 7.47 (d, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, free indole H7), 7.39 (t, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, bound indolyl H6), 7.30 (t, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H, bound indolyl H5), 7.09 (t, \(^3\)J\(_{HH}\) = 7.8 Hz, 1H,
free indole H6), 6.96 (t, $^3J_{HH} = 7.8$ Hz, 1H, free indole H5), 6.78 (d, $^3J_{HH} = 7.8$ Hz, 1H, free indole H4), 6.47 (d, $^3J_{HH} = 1.8$ Hz, 1H, imidazolyl H4), 5.47 (d, $^3J_{HH} = 1.8$ Hz, 1H, imidazolyl H5), 5.42 (s, 1H, CH), 2.32 (s, 3H, imidazolyl CH$_3$), 2.16 (s, 3H, bound indolyl CH$_3$), 2.12 (s, 3H, free indole CH$_3$), 1.53 (t, $^3J_{HH} = 8.4$ Hz, 3H, CH$_2$CH$_2$), 1.26 (t, $^3J_{HH} = 8.4$ Hz, 3H, CH$_2$CH$_3$), 0.69-0.55 (m, 4H, CH$_2$CH$_3$), 0.32 (s, 1H, CH), 2.36 (br s, CH$_2$CH$_3$), 0.75 (br s, CH$_2$CH$_3$).

$^1$H NMR (CDCl$_3$, 600 MHz): δ 7.89 (br s, 1H, NH), 7.56 (d, $^3J_{HH} = 7.8$ Hz, 1H, bound indolyl H7), 7.43 (d, $^3J_{HH} = 7.8$ Hz, 2H, bound indolyl H4, free indole H7 overlap), 7.11 (t, $^3J_{HH} = 7.8$ Hz, 1H, bound indolyl H6), 7.03-7.01 (m, 4H bound indolyl H5, free indole H6, free indole H5, free indole H4 overlap), 7.00 (d, $^3J_{HH} = 1.8$ Hz, 1H, imidazolyl H4), 6.63 (d, $^3J_{HH} = 1.8$ Hz, 1H, imidazolyl H5), 5.94 (s, 1H, CH), 3.53 (s, 3H, imidazolyl CH$_3$), 2.45 (s, 3H, bound indolyl CH$_3$), 2.28 (s, 3H, free indole CH$_3$), 1.23 (t, $^3J_{HH} = 7.8$ Hz, 3H, CH$_2$CH$_3$), 0.82 (t, $^3J_{HH} = 7.8$ Hz, 3H, CH$_2$CH$_3$), 0.322 (dq, 1H, $^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 8.4$ Hz, CH$_2$CH$_3$), 0.260 (dq, 1H, $^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 8.4$ Hz, CH$_2$CH$_3$), 0.141 (q, $^3J_{HH} = 7.8$ Hz, 2H, CH$_2$CH$_3$). $^{13}$C{$_1$H} NMR (CDCl$_3$, 150.8 MHz): δ
148.40 (s, imidazolyl C2), 142.88 (s, bound indolyl C3a), 135.94 (s, free indole C7a), 134.64 (s, bound indolyl C2), 130.69 (s, bound indolyl C7a), 130.01 (s, free indole C2), 129.00 (s, free indole C3a), 123.61 (s, imidazolyl C4), 122.49 (s, free indole C6), 122.47 (s, imidazolyl C5), 120.26 (s, bound indolyl C6), 119.43 (s, free indole C5), 118.60 (s, bound indolyl C5), 118.10 (s, free indole C4), 113.54 (s, bound indolyl C7), 110.74 (s, free indole C3), 33.74 (s, imidazolyl CH2), 32.41 (s, CH), 9.50 (s, CH3), 9.38 (s, CH2), 1.35 (br s, CH2), –0.43 (br s, CH3), 9.01 (s, CH2). Anal. Calcd for C27H31N4Al: C, 73.95; H, 7.13; N, 12.78. Found: C, 72.62; H, 7.59; N, 12.42.

**Synthesis of (1-CH3-2-C3H2N2)HC(3-CH3C8H4NH)(3-CH3C8H4N)-Al-{CH2CH(CH3)2}2 (2c)**

A solution of tri-*iso*-butylaluminum (0.297 g, 1.50 mmol) in 10 mL of toluene was added via cannula to a suspension of 1 (0.531 g, 1.50 mmol) in freshly distilled toluene (20 mL). A clear yellow solution resulted immediately. The solution was stirred at 25 °C for 2 h and stored at –30 °C for 48 h. A white, needle-like, crystalline solid was isolated by filtration through a medium Schlenk frit. The solid was recrystallized from hot toluene (5 mL) to yield crystalline 2c as a toluene solvate (~ 0.50 C7H8). Yield: 0.42 g, 54%. 1H NMR (CDCl3, 400 MHz): δ 7.91 (br s, 1H, NH), 7.58 (d, JHH = 8.4 Hz, 1H, bound indolyl H7), 7.45 (d, JHH = 6.4 Hz, 1H, free indole H7), 7.44 (d, JHH = 6.8 Hz, 1H, bound indolyl H4), 7.12 (d, JHH = 1.2 Hz, 1H, imidazolyl H4) 7.17- 7.10 (m, 1H, bound indolyl H6), 7.05-6.99 (m, 4H, bound indolyl H5, free indole H4, H5 and H6 overlap), 6.81 (d, JHH = 1.2 Hz, 1H, imidazolyl H5), 6.01 (s, 1H, CH), 3.69 (s, 3H,
imidazolyl CH, 2.49 (s, 3H, bound indolyl CH), 2.29 (s, 3H, free indole CH), 1.54 (m, 1H, CH$_2$CH(CH$_3$)$_2$), 1.03 (d, $^3J_{HH}$ = 7.6 Hz, 3H, CH$_2$CH(CH$_3$)$_2$), 1.02 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$_2$CH(CH$_3$)$_2$), 0.62 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$_2$CH(CH$_3$)$_2$), 0.432 (dd, $^3J_{HH}$ = 14.4 Hz, 1H, C$_2$H$_2$CH(CH$_3$)$_2$), 0.348 (dd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, C$_2$H$_2$CH(CH$_3$)$_2$), 0.312 (dd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, C$_2$H$_2$CH(CH$_3$)$_2$), 0.215 (dd, $^3J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, C$_2$H$_2$CH(CH$_3$)$_2$).

$^{13}$C NMR (CDCl$_3$, 100.6 MHz):

$^\delta$ 148.32 (s, imidazolyl C2), 142.83 (s, bound indolyl C3a), 135.94 (s, free indole C7a), 134.21 (s, bound indolyl C2), 130.81 (s, bound indolyl C7a), 130.04 (s, free indole C2), 129.02 (s, free indole C3a), 123.97 (s, imidazolyl C4), 122.50 (s, free indole C4), 121.13 (s, bound indole C6), 119.42 (s, free indole C5), 118.63 (s, bound indolyl C5), 117.99 (s, free indole C7), 117.73 (s, bound indolyl C4), 113.91 (s, bound indolyl C7), 110.76 (s, free indole C4), 108.72 (s, bound indolyl C3), 105.84 (s, free indole C3), 33.99 (s, imidazolyl CH$_3$), 32.47 (s, CH), 28.47 (s, CH$_2$CH(CH$_3$)$_2$), 28.44 (s, CH$_2$CH(CH$_3$)$_2$), 27.83 (s, CH$_2$CH(CH$_3$)$_2$), 27.79 (s, CH$_2$CH(CH$_3$)$_2$), 26.37 (s, CH$_2$CH(CH$_3$)$_2$), 26.02 (s, CH$_2$CH(CH$_3$)$_2$), 24.51 (br s, CH$_2$CH(CH$_3$)$_2$), 21.83 (br s, CH$_2$CH(CH$_3$)$_2$), 9.51 (s, bound indolyl CH$_3$), 9.06 (s, free indole CH$_3$).

$^1$H NMR (C$_6$D$_6$, 400 MHz): $^\delta$ 8.05 (br s, 1H, NH), 8.04 (d, $^3J_{HH}$ = 7.8 Hz, 1H, bound indolyl H7), 7.74 (d, $^3J_{HH}$ = 7.8 Hz, 1H, bound indolyl H4), 7.50 (d, $^3J_{HH}$ = 7.6 Hz, 1H, free indole H7), 7.42 (t, $^3J_{HH}$ = 7.8 Hz, 1H, bound indolyl H5), 7.32 (t, $^3J_{HH}$ = 7.8 Hz, 1H, bound indolyl H5), 7.13-7.12 (m, aromatics), 7.06-7.00 (m, 2H, aromatics), 6.95-6.93 (d, 1H, aromatics), 6.61 (d, $^3J_{HH}$ = 1.6 Hz, 1H, imidazolyl H4), 5.57 (d, $^3J_{HH}$ = 1.6 Hz, 1H, imidazolyl H5), 5.52 (s, 1H, CH), 2.35 (s, 3H, imidazolyl CH$_3$), 2.29 (m, 1H,
CH$_2$CH(CH$_3$)$_2$, 2.19 (s, 3H, bound indolyl CH$_3$), 2.14 (s, 3H, free indole CH$_3$), 1.94 (m, 1H, CH$_2$CH(CH$_3$)$_2$), 1.25 (d, $^3$J$_{HH}$ = 6.4 Hz, 3H, CH$_2$CH(CH$_3$)$_2$), 1.23 (d, $^3$J$_{HH}$ = 6.4 Hz, 3H, CH$_2$CH(CH$_3$)$_2$), 0.97 (d, $^3$J$_{HH}$ = 2.4 Hz, 3H, CH$_2$CH(CH$_3$)$_2$), 0.95 (d, $^3$J$_{HH}$ = 2.4 Hz, 3H, CH$_2$CH(CH$_3$)$_2$), 0.79 (dd, $^2$J$_{HH}$ = 14.4 Hz, $^3$J$_{HH}$ = 7.2 Hz, 1H, CH$_2$CH(CH$_3$)$_2$), 0.70 (dd, $^2$J$_{HH}$ = 14.0 Hz, $^3$J$_{HH}$ = 6.8 Hz, 1H, CH$_2$CH(CH$_3$)$_2$), 0.64 (dd, $^2$J$_{HH}$ = 14.4 Hz, $^3$J$_{HH}$ = 6.8 Hz, 1H, CH$_2$CH(CH$_3$)$_2$), 0.60 (dd, $^2$J$_{HH}$ = 14.0 Hz, $^3$J$_{HH}$ = 7.2 Hz, 1H, CH$_2$CH(CH$_3$)$_2$).

Anal. Calcd for C$_{31}$H$_{39}$N$_4$Al•0.50 C$_7$H$_8$: C, 76.60; H, 8.01; N, 10.38. Found: C, 74.20; H, 8.62; N, 10.05.

**Synthesis of (1-CH$_3$-2-C$_3$H$_2$N$_2$)HC(3-CH$_3$C$_8$H$_4$NH)(3-CH$_3$C$_8$H$_4$N)Al{C(CH$_3$)$_3$)$_2$ (2d)**

A solution of tri-tert-butylaluminum (0.297 g, 1.50 mmol) in 15 mL of toluene was added via cannula to a suspension of 1 (0.531 g, 1.50 mmol) in freshly distilled toluene (20 mL). A clear yellow solution resulted immediately. The solution was heated under reflux for 20 h and then stirred at 25 °C for 4 h. A cream colored solid was observed. The solution was stored at –30 °C overnight. A white solid was isolated by filtration through a fine Schlenk frit. The filtrate was concentrated to half the original volume and kept at –30 °C overnight. A second crop was isolated by filtration through a fine Schlenk frit. The two crops were combined and recrystallized from hot toluene (10 mL) to yield 2d as a toluene solvate (~ 0.88 C$_7$H$_8$). Yield: 0.60 g, 70%. $^1$H NMR (CDCl$_3$, 600 MHz): δ 7.84 (br s, 1H, NH), 7.71 (d, $^3$J$_{HH}$ = 8.4 Hz, 1H, bound indolyl H7), 7.45 (d, $^3$J$_{HH}$ = 8.4 Hz, 1H, bound indolyl H4), 7.42 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H, free indole H7), 7.24 (d, $^3$J$_{HH}$ = 1.8 Hz, 1H, imidazolyl H4), 7.16 (t, $^3$J$_{HH}$ = 8.4 Hz, 1H, bound indolyl H6), 7.12 (t, $^3$J$_{HH}$ = 8.4 Hz, 1H, bound indolyl H5), 7.04-7.01 (m, 3H, aromatics), 6.95 (m, 1H,
imidazolyl H4), 6.86 (d, $^3J_{HH} = 1.8$ Hz, 1H, imidazolyl H5), 6.04 (s, 1H, CH), 3.68 (s, 3H, imidazolyl CH$_3$), 2.56 (s, 3H, bound indolyl CH$_3$), 2.24 (s, 3H, free indole CH$_3$), 1.33 (s, 9H, C(CH$_3$)$_3$), 0.58 (s, 9H, C(CH$_3$)$_3$).  $^{13}$C $^{1}$H NMR (CDCl$_3$, 100.6 MHz): $^\delta$ 148.53 (s, imidazolyl C2), 143.19 (s, bound indolyl C3a), 136.02 (s, free indole C7a), 135.04 (s, bound indolyl C2), 131.26 (s, bound indolyl C7a), 129.98 (s, free indole C2), 128.27 (s, free indole C3a), 124.66 (s, imidazolyl C4), 122.51 (s, free indole C6, imidazolyl C5 overlap), 119.92 (s, bound indolyl C6), 119.43 (s, free indole C5), 118.71 (s, bound indolyl C5), 118.26 (s, free indole C7), 117.53 (s, bound indolyl C4), 115.12 (s, bound indolyl C7), 110.76 (s, free indole C4), 109.85 (s, bound indolyl C3), 105.64 (s, free indole C3), 34.23 (s, imidazolyl CH$_3$), 32.83 (s, CH), 31.76 (s, C(CH$_3$)$_3$), 30.47 (s, C(CH$_3$)$_3$), 16.25 (br s, C(CH$_3$)$_3$), 15.28 (br s, C(CH$_3$)$_3$), 9.90 (s, indolyl CH$_3$), 9.14 (s, indolyl CH$_3$).

$^1$H NMR (C$_6$D$_6$, 600 MHz ): $^\delta$ 8.18 (d, $^3J_{HH} = 8.4$ Hz, 1H, bound indolyl H7), 7.94 (br s, 1H, NH), 7.69 (d, $^3J_{HH} = 8.4$ Hz, 1H, bound indolyl H4), 7.48 (d, $^3J_{HH} = 7.8$ Hz, 1H, free indole H7), 7.42 (t, $^3J_{HH} = 8.4$ Hz, 1H, bound indolyl H6), 7.30 (t, $^3J_{HH} = 8.4$ Hz, 1H, bound indolyl H5), 7.10 (t, $^3J_{HH} = 7.8$ Hz, 1H, free indole H6), 6.95 (t, $^3J_{HH} = 7.8$ Hz, 1H, free indole H5 ), 6.80 (s, 1H, imidazolyl H5), 6.76 (d, $^3J_{HH} = 7.8$ Hz, 1H, free indole H4), 5.59 (s, 2H, imidazolyl H4, CH overlap), 2.28 (s, 3H, imidazolyl CH$_3$), 2.19 (s, 3H, bound indolyl CH$_3$), 2.18 (s, 3H, free indole CH$_3$) 1.58 (s, 9H, C(CH$_3$)$_3$), 1.04 (s, 9H, C(CH$_3$)$_3$).
Synthesis of (1-CH$_3$-2-C$_3$H$_2$N$_2$)HC(3-CH$_3$C$_8$H$_4$NH)(3-CH$_3$C$_8$H$_4$N)Ga{C(CH$_3$)$_3$}$_2$ (3)

A solution of tri-tert-butylgallium (0.360 g, 1.50 mmol) in 10 mL of toluene was added via cannula to a suspension of 1 (0.531 g, 1.50 mmol) in freshly distilled toluene (20 mL). A clear yellow solution resulted immediately. The solution was heated under reflux for 20 h and then cooled to 25 °C. The solution was then kept at –30 °C overnight. A cream colored solid was isolated by filtration through a fine Schlenk frit. The filtrate was concentrated to half the original volume and kept at –30 °C overnight. A second crop was isolated by filtration through a fine Schlenk frit. The two crops were combined and recrystallized from hot toluene (10 mL) to yield a microcrystalline white solid 3 as a toluene solvate (~ 0.50 C$_7$H$_8$). Yield: 0.35 g, 61%. $^1$H NMR (CDCl$_3$, 600 MHz): δ 7.97 (br s, 1H, NH), 7.56 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H, bound indolyl H7), 7.44 (d, $^3$J$_{HH}$ = 7.2 Hz, 2H, free indole H7, bound indolyl H4 overlap), 7.16 (t, $^3$J$_{HH}$ = 7.8 Hz, 1H, bound indolyl H6), 7.14 (d, $^3$J$_{HH}$ = 1.2 Hz, 1H, imidazolyl H4), 7.10-6.96 (m, 5H, aromatics including toluene), 6.95 (d, $^3$J$_{HH}$ = 1.2 Hz, 1H, imidazolyl H5), 6.05 (s, 1H, CH), 3.79 (s, 3H, imidazolyl CH$_3$), 2.54 (s, 3H, bound indolyl CH$_3$), 2.29 (s, 3H, free indole CH$_3$), 1.44 (s, 9H, C(CH$_3$)$_3$), 0.63 (s, 9H, C(CH$_3$)$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$, 100.6 MHz): δ 147.55 (s, imidazolyl C2), 143.79 (s, bound indolyl C3a), 135.93 (s, free indole C7a), 135.73 (s, bound indolyl C2), 130.89 (s, bound indolyl C7a), 130.83 (s, free indole C2), 129.01 (s, free indole C3a), 125.06 (s, imidazolyl C4), 122.26 (s, free indole C6), 122.12 (s, imidazolyl C5), 119.49 (s, bound indolyl C6), 119.29 (s, free indolyl C5), 118.61 (s, bound indolyl C5), 117.64 (s, free indole C7), 117.51 (s, bound indolyl C4), 115.02 (s, bound indolyl C7), 110.71 (s, free indole C4), 108.91 (s, bound indolyl C3), 105.15 (s, free indole C3), 34.11 (s, imidazolyl CH$_3$), 32.56 (s, CH), 31.78 (s, C(CH$_3$)$_3$), 30.40 (s,
C(CH₃)₅, 23.78 (br s, C(CH₃)₅), 22.29 (br s, C(CH₃)₅), 9.79 (s, bound indolyl CH₃), 9.27 (s, free indole CH₃).

¹H NMR (C₆D₆, 600 MHz): δ 8.07 (br s, 1H, NH), 8.00 (d, ³JHH = 7.8 Hz, 1H, bound indolyl H7), 7.75 (d, ³JHH = 7.8 Hz, 1H, bound indolyl H4), 7.49 (d, ³JHH = 7.8 Hz, 1H, free indole H7), 7.42 (t, ³JHH = 7.8 Hz, 1H, bound indolyl H6), 7.31 (t, ³JHH = 7.8 Hz, 1H, bound indolyl H5), 7.05 (t, ³JHH = 7.8 Hz, 1H, free indole H6), 6.97 (t, ³JHH = 7.8 Hz, 1H, free indole H5), 6.79 (d, ³JHH = 7.8 Hz, 1H, free indole H4), 6.66 (d, ³JHH = 1.2 Hz, 1H, imidazolyl H4), 5.67 (d, ³JHH = 1.2 Hz, 1H, imidazolyl H5), 5.66 (s, 1H, CH), 2.37 (s, 3H, imidazolyl CH₃), 2.27 (s, 3H, bound indolyl CH₃), 2.18 (s, 3H, free indole CH₃), 1.60 (s, 9H, C(CH₃)₅), 1.00 (s, 9H, C(CH₃)₅). Anal. Calcd for C₃₁H₇₉N₅Ga•0.40 C₇H₈: C, 70.63; H, 7.40; N, 9.79. Found: C, 70.47; H, 8.13; N, 9.69.

**Synthesis of (1-CH₃-2-C₃H₂N₂)HC(3-CH₃C₈H₄N)₂Al₂(CH₃)₄ (4a)**

Slightly more than two equivalents of trimethylaluminum (1.8 mL, 3.6 mmol, 2.0 M solution in toluene) was added via syringe to a stirred suspension of 1 (0.531 g, 1.50 mmol) in freshly distilled toluene (30 mL). A clear yellow solution resulted immediately and after 0.5 h the color had darkened. The solution was stirred at 25 °C for 2 h, concentrated to about 20 mL in vacuo and kept at −30 °C overnight. A yellow crystalline solid was isolated by filtration through a fine Schlenk frit (yield: 0.687 g). The filtrate was concentrated in vacuo to half the original volume and stored at −5 °C overnight. A second crop was isolated by filtration through a fine Schlenk frit. The two crops were combined and recrystallized from hot toluene (10 mL) to yield 4a as a toluene solvate (~ 0.91 C₇H₈). Yield: 0.55 g, 66%. ¹H NMR (CDCl₃, 600 MHz): δ 7.64 (d, ³JHH = 7.6 Hz,
$^1$H, bridging indolyl H7), 7.49 (d, $^3J_{HH} = 7.2$ Hz, 2H, bound indolyl H7, bound indolyl H4, overlap), 7.35-7.27 (m, 3H, bridging indolyl H5, bridging indolyl H6, bound indolyl H6, overlap), 7.02-6.95 (m, 2H, bridging indolyl H4, bound indolyl H5, overlap), 6.97 (d, $^3J_{HH} = 1.8$ Hz, 1H, imidazolyl H5), 6.88 (d, $^3J_{HH} = 1.8$ Hz, 1H, imidazolyl H4), 5.94 (s, 1H, CH), 3.67 (s, 3H, imidazolyl CH$_3$) 2.56 (s, 3H, indolyl CH$_3$), 2.30 (s, 3H, indolyl CH$_3$), –0.28 (s, 3H, CH$_3$), –0.58 (s, 3H, CH$_3$), –1.51 (s, 3H, CH$_3$), –1.95 (s, 3H, CH$_3$).

$^{13}$C{$^1$H} NMR (CDCl$_3$, 100.6 MHz): δ 148.24 (s, imidazolyl C2), 145.19 (s, bound indolyl C3a), 143.45 (s, bridging indolyl C7a), 137.85 (s, bridging indolyl C2), 136.27 (s, bridging indolyl C3a), 135.70 (s, bound indolyl C2), 130.52 (s, bound indolyl C7a), 124.38 (s, bridging indolyl C6), 124.18 (s, imidazolyl C5), 122.88 (s, bound indolyl C6), 122.18 (s, imidazolyl C4), 122.03 (s, bridging indolyl C3), 120.88 (s, bridging indolyl C4), 119.57 (s, bound indolyl C7), 118.16 (s, bound indolyl C5), 117.90 (s, bound indolyl C4), 117.49 (s, bridging indolyl C7), 114.13 (s, bridging indolyl C5), 105.93 (s, bound indolyl C3), 34.47 (s, imidazolyl CH$_3$), 34.40 (s, CH), 10.23 (s, indolyl CH$_3$), 9.14 (s, free CH$_3$), –5.84 (br s, CH$_3$), –9.52 (br s, CH$_3$), –10.26 (br s, CH$_3$), –13.87 (br s, CH$_3$).

**Synthesis of (1-CH$_3$-2-C$_3$H$_2$N$_2$)HC(3-C$_3$H$_2$C$_2$H$_4$N)$_2$Al$_2$(C$_2$H$_5$)$_4$ (4b)**

A solution of triethylaluminum (0.322 g, 2.82 mmol) in 10 mL of toluene was added via cannula to a suspension of 1 (0.500 g, 1.41 mmol) in freshly distilled toluene (20 mL). A clear yellow solution resulted immediately. The solution was stirred for 2 h at 25 °C and then stored at –30 °C overnight. A white solid was isolated by filtration through a fine Schlenk frit. The filtrate was concentrated to half the original volume and stored at –30 °C overnight. The process was repeated and a total of 3 crops were isolated.
The product from all three crops was combined and recrystallized from hot toluene (10 mL) yielding 4b as a toluene solvate (~0.50 C7H8). Yield: 0.35 g, 44%. $^1$H NMR (CDCl$_3$, 600 MHz): δ 7.72 (d, $^3$J$_{HH}$ = 7.8 Hz, 1H, bridging indolyl H7), 7.49-7.45 (m, 2H, bound indolyl H7, bound indolyl H4, overlap), 7.38-7.30 (m, 3H, bridging indolyl H5, bridging indolyl H6, bound indolyl H6, overlap), 7.02 (m, 1H, bridging indolyl H4), 7.01 (d, $^3$J$_{HH}$ = 1.8 Hz, 1H, imidazolyl H4), 6.99 (m, 1H, bound indolyl H5), 6.89 (d, $^3$J$_{HH}$ = 1.8 Hz, 1H, imidazolyl H5), 5.91 (s, 1H, CH), 3.68 (s, 3H, imidazolyl CH$_3$) 2.57 (s, 3H, indolyl CH$_3$), 2.30 (s, 3H, indolyl CH$_3$), 1.19 (t, $^3$J$_{HH}$ = 8.4 Hz, 3H, CH$_2$CH$_3$), 0.49 (m, 1H, CH$_2$CH$_3$), 0.24 (m, 1H, CH$_2$CH$_3$), 0.20 (t, $^3$J$_{HH}$ = 8.4 Hz, 3H, CH$_2$CH$_3$), −0.06 (m, 1H, CH$_2$CH$_3$), −0.29 (t, $^3$J$_{HH}$ = 8.4 Hz, 3H, CH$_2$CH$_3$), −1.17 (m, 1H, CH$_2$CH$_3$), −1.32 (m, 1H, CH$_2$CH$_3$). $^{13}$C{$^1$H} NMR (CDCl$_3$, 150.8 MHz): δ 148.46 (s, imidazolyl C2), 144.91 (s, bound indolyl C3a), 143.90 (s, bridging indolyl C7a), 138.09 (s, bridging indolyl C2), 136.53 (s, bridging indolyl C3a), 135.96 (s, bound indolyl C2), 130.45 (s, bound indolyl C7a), 124.38 (s, bridging indolyl C6), 124.09 (s, imidazolyl C5), 124.00 (s, bound indolyl C6), 119.55 (s, bound indolyl C7), 117.96 (s, bound indolyl C5), 117.84 (s, bound indolyl C4), 117.37 (s, bridging indolyl C7), 114.23 (s, bridging indolyl C5), 105.80 (s, free indolyl C3), 34.65 (s, imidazolyl CH$_3$), 34.48 (s, CH), 10.28 (s, bound indolyl CH$_3$), 9.73 (s, CH$_2$CH$_3$), 9.41 (s, CH$_2$CH$_3$), 9.19 (s, free indolyl CH$_3$), 8.42 (s, CH$_2$CH$_3$), 7.48 (s, CH$_2$CH$_3$), 2.44 (br s, CH$_2$CH$_3$), 0.35 (br s, CH$_2$CH$_3$), −0.43 (br s, CH$_2$CH$_3$), −4.17 (br s, CH$_2$CH$_3$). Anal. Calcd for C$_{31}$H$_{46}$N$_4$Al$_2$: C, 71.24; H, 7.71; N, 10.72. Found: C, 66.90; H, 8.14; N, 10.17.
X-ray Crystallography

Crystals of 1 were grown by Laura Seig by slow cooling to –30 °C a saturated solution of 1 in a methylene chloride (50%) and THF (50%) mixture. Data collection, structure solution, and refinement for 1 were performed by Nicholas Kingsley. Crystals of 2d•C7H8 and 3•C7H8 were obtained from toluene by slowly cooling the reaction filtrates at –30 °C. X-ray diffraction data were collected on a Siemens three-circle platform diffractometer equipped with a 2K CCD detector. The frame data were acquired with the SMART software using Mo Kα radiation (λ = 0.710 73 Å). Cell constants were determined with SAINT from the complete dataset. A complete sphere was scanned on ω (0.3°) with run times of 30s/frame for 2d•C7H8. A total of 1265 frames were collected for the dataset. For 3•C7H8 a complete hemisphere was scanned on ω (0.3°) with run times of 60s/frame. A total of 1271 frames were collected for the dataset. An additional 50 frames, identical to the first 50 frames were collected for each data set to determine crystal decay. The frames were integrated using the SAINT software and the data were corrected for absorption and decay using the SADABS program. The structures were solved by direct methods using SHELXS-97 and refined by least-squares methods on R2 using SHELXL-97. All hydrogen atoms were calculated and put on idealized positions. Indolyl carbon C36 in 3•C7H8 was disordered over two positions with equal occupancy. Details of data collection and refinement and unit cell parameters for 1, 2d•C7H8 and 3•C7H8 are provided in Table 1.
Table 3.1. Summary of X-ray Crystallographic Data

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a \( I > 2σ(I) \).  
b \( R₁ = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \).  
c \( wR₂ = \left[ \frac{\sum w (F_o^2 - F_c^2)^2}{\sum w (F_o^2)^2} \right]^{1/2} \).
3.3 Results and discussion

3.3.1 Synthesis and characterization of di(3-methylindolyl)imidazolylmethane (1)

The synthesis of 1 was achieved using a procedure analogous to the synthesis of other di(3-methylindolyl)methanes reported by Pindur and the Mason group. The first preparation of 1 was carried out by undergraduate researcher Laura Seig using acid-catalyzed condensation of one equivalent of N-methylimidazole-2-carbaldehyde with two equivalents of 3-methylindole. Seig characterized 1 by NMR spectroscopy and successfully grew X-ray quality crystals. Here we report details of the refined synthesis and complete characterization of 1 including 2-D NMR spectroscopic and crystallographic characterization.

One equivalent of N-methylimidazole-2-carbaldehyde was added to a solution of two equivalents of 3-methylindole in absolute ethanol. To catalyze the reaction 5 mL of concentrated H$_2$SO$_4$ was added. The solution was refluxed for 1.5 h and [1•H][HSO$_4$] was isolated as a white solid by filtration (eq 1). During initial attempts to synthesize [1•H][HSO$_4$], a smaller amount of H$_2$SO$_4$ (about 20 drops for the reaction scale reported here) was used. This resulted in longer reaction times, lower yield and usually a mixture of product and starting materials. Subsequently it was observed that increasing the amount of H$_2$SO$_4$ resulted in shorter reaction time and isolation of almost pure [1•H][HSO$_4$] in 42% yield.

The $^1$H NMR spectrum of [1•H]$^-$ in DMSO-$d_6$ shows a broad resonance at 10.84 ppm corresponding to the indole NH. There are also two broad singlets at 7.74 ppm and 7.55 ppm each integrating to one hydrogen. These correspond to the imidazolyl H4 and H5 respectively. These assignments were made on the basis of imidazolyl chemical shifts.
reported by Breitmaier\textsuperscript{22} and coworkers. The broadening of the resonances may be attributed to the exchangeable proton. In the aromatic region there are two doublets (indolyl H7 and H4) and two triplets (indolyl H5 and H6) each integrating to two hydrogens. There is a singlet methine resonance at 6.60 ppm, one singlet (3H) at 3.50 ppm corresponding to the imidazolyl CH\textsubscript{3}, and a singlet at 2.11 ppm (6H) corresponding to the two chemically equivalent methyls on the two indoles. Integration confirms two indoles per imidazole. For comparison, the resonance for the methyl on free N-methylimidazole-2-carbaldehyde appears at 3.91 ppm and the methyl on free 3-methylindole appears at 2.24 ppm in DMSO-\textit{d}$_6$.

Deprotonation of the imidazole nitrogen was carried out by adding Amberlite IRA-67 ion exchange resin to a suspension of [1\textsuperscript{•}H][HSO\textsubscript{4}] in acetonitrile (eq 2). As observed for the pyridyl analog of 1,\textsuperscript{1} the protonated ligand is very sparingly soluble in acetonitrile. But on neutralization, 1 is soluble. This allows us to start with a suspension of [1\textsuperscript{•}H]\textsuperscript{+} thereby reducing the use of solvent by two-thirds from that reported by Fneich.\textsuperscript{1} Amberlite IRA-67 has an ion exchange capacity of 1.6 meq/mL, therefore it can be stoichiometrically added to a reaction mixture to achieve deprotonation. Thus the amount
of Amberlite was reduced from that previously reported by Fneich in the synthesis of di(3-methylindolyl)pyridylmethane.

The characterization of 1 was carried out by NMR (1D and 2D) spectroscopy, X-ray crystallography, HRMS and elemental analysis. The m/z measured for the protonated molecular ion C_{23}H_{23}N_{4} (M+H^+) obtained by high resolution mass spectroscopy (ES) was 355.1922, which equals the calculated value. The results for elemental analysis for C_{23}H_{22}N_{4} were also as expected.

\begin{equation}
\text{CH}_3\text{CN} \quad \text{Amberlite IRA-67} \\
\text{NH} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{HN} \\
\text{H}_3\text{C} \quad \text{NH} \quad \text{HN} \quad \text{CH}_3\text{H} \quad \text{N} \\
\text{NH} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{HN} \quad \text{CH}_3\text{N} \\
\end{equation}

The $^1$H NMR spectrum of 1 in chloroform-$d$ at 600 MHz shows a broad peak at 9.41 ppm corresponding to two indolyl NH protons. There are two distinct doublets at 7.47 ppm and 7.28 ppm corresponding to indole H7 and H4, and two triplets at 7.10 ppm and 7.07 ppm corresponding to the indole H5 and H6, respectively. The specific assignments were made on the basis of gCOSY experiments (Figure 3.2) which confirms the connectivity as H7–H6–H5–H4. The doublet at 7.47 ppm was assigned H7 on the basis of previous work by Mason$^5$ and coworkers. The imidazolyl H4 and H5 resonances show up as sharp doublets with $^3J_{HH} = 1.2$ Hz at 7.09 ppm and 6.77 ppm respectively. These assignments were made on the basis of imidazolyl chemical shifts reported by
Breitmaier and coworkers. They reported $^3J_{HH} = 1.3$ Hz for such systems. An important feature is that the resonances for the imidazolyl protons in 1 are considerably sharp and shifted upfield as compared to the corresponding ones in the protonated ligand. This may be attributed to the lack of the exchangeable proton. There is a singlet resonance at 3.69 ppm corresponding to the methyl on imidazole and a resonance at 2.39 ppm

![Figure 3.2. gCOSY spectrum of 1 in chloroform-$d$ from 6.2 ppm to 8.0 ppm]
corresponding to the methyl substituents on the indoles. The $^1$H NMR spectrum of 1 in DMSO-$d_6$ is also well resolved and exhibits similar attributes. The $^1$H NMR spectrum of 1 in benzene-$d_6$ is not well-resolved in the aromatic region.

The resonances in the $^{13}$C NMR spectrum were assigned on the basis of HMQC (Heteronuclear Multiple Quantum Coherence) and HMBC (Heteronuclear Multiple Bond Coherence) experiments.\textsuperscript{23b} HMQC gives cross-peaks for direct C–H couplings while HMBC gives cross-peaks for long range (2-4 bond) C–H coupling. The assigned chemical shifts are consistent with those previously reported by Mason\textsuperscript{5} and coworkers for other di- and tri-indolylmethanes with the exception that the assignments for C4 and C7 are interchanged.

X-ray crystallographic data further confirmed the molecular structure of 1. Crystals of 1 were grown by Laura Seig from a saturated solution of 1 in methylene chloride (50%) and THF (50%). The data collection and structure solution of 1 were performed by Nicholas Kingsley. The ORTEP diagram is shown in Figure 3.3 and selected bond distances and angles are presented in Table 3.2.

The molecule crystallized in space group P-1 and the structure was refined with an $R_1$ factor of 5.66\% (see Table 3.1). Bond distances and angles within the indolyl moieties compare favorably with the reported literature values for other diindolyl methane ligands.\textsuperscript{5} The distance between atoms N3 and N1 is 3.0502(2) Å and the distance between N2 and N1 is 3.2802(3) Å. Some N---N distances reported for NH---N bonds are 3.234(1) Å,\textsuperscript{24a} 3.07 Å,\textsuperscript{24b} 3.052(1) Å,\textsuperscript{24a} 2.67(2) Å,\textsuperscript{24c} and 2.637 Å.\textsuperscript{24d} Thus we can say that there is hydrogen bonding between the imidazolyl nitrogen and the indolyl NH.
Figure 3.3. ORTEP diagram of 1. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, except indole NH, are omitted for clarity

Table 3.2. Selected bond distances and angles for 1.

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3.3.2 Preparation of bidentate complexes of 1

We set out to investigate the reactivity of 1 with aluminum and gallium alkyls with the aim of generating tridentate monoalkyl complexes analogous to the series of complexes 5a-d synthesized by Fneich.\(^1\) Contrary to our initial expectations we isolated a series of bidentate dialkyl complexes of the formula HLMR\(_2\) (LH\(_2\) = 1). Reaction of one equivalent of MR\(_3\) (M = Al, R = Me, Et, \(^t\)Bu or \(^t\)Bu; M = Ga, R = \(^t\)Bu) with 1 produces a series of bidentate aluminum complexes 2a-d and gallium complex 3 (eq 3). The complex 2a is a white powdery solid, 2b is yellow, 2c and 3 are white crystalline solids while 2d is an off-white powder.

Complexes 2a–d and 3 were characterized by \(^1\)H and \(^{13}\)C NMR spectroscopy. The complexes 2b, 2c and 3 were characterized by elemental analysis. X-ray crystallographic characterization was carried out for 2d and 3. Additionally, 2b was extensively characterized by 2-D NMR techniques gCOSY, HMQC and HMBC. \(^1\)H and \(^{13}\)C NMR chemical shift values for complexes 2a-d and 3 were very similar, hence assignments were made by comparison to those for 2b. Another point to note is that the \(^1\)H NMR
spectra are much more resolved in the aromatic region in benzene-$d_6$ than in chloroform-$d$. NMR data is reported in both solvents in the experimental section.

We begin by discussing the $^1$H NMR spectra of these complexes in the aromatic region. The $^1$H NMR spectrum of \( \text{2b} \) in benzene-$d_6$ exhibits a broad resonance at 7.99 ppm corresponding to the NH on the free uncoordinated indole arm. There are four distinct doublets at 8.00 ppm, 7.71 ppm, 7.47 ppm and 6.78 ppm each integrating to one hydrogen. There are also four distinct triplets at 7.39 ppm, 7.30 ppm, 7.09 ppm and 6.96 ppm each integrating to one hydrogen. Thus, we infer that the two indole moieties of \( \text{1} \) are in different chemical environments. The presence and integration of the NH resonance indicates that only one of the indole moieties is uncoordinated and protonated. The doublet resonances at 8.00 ppm and 7.71 ppm correspond to H7 and H4, respectively, on the bound indolyl. The doublet resonances at 7.47 ppm and 6.78 ppm correspond to the H7 and H4 on the free indole. The triplet resonances at 7.39 ppm and
7.30 ppm are assigned to H6 and H5 on the bound indolyl substituents, whereas the
triplet resonances at 7.09 ppm and 6.96 ppm correspond to H6 and H5 on the free indole
substituent. There are two doublets at 6.47 ppm and 5.47 ppm each with a coupling
constant $^{3}J_{HH} = 1.8$ Hz, indicating that these correspond to imidazolyl protons H4 and H5,
respectively. As discussed for 1, these resonances are assigned on the basis of the
chemical shifts reported by Breitmaier and coworkers. There is a single methine
resonance at 5.42 ppm indicating the formation of a single species as opposed to a
mixture. Similar trends are observed for resonances in the aromatic region for all
complexes 2a-d and 3. A portion of the aromatic region of the $^1$H NMR spectrum for 2b
in benzene-$d_6$ is shown in Figure 3.4.

Figure 3.4. $^1$H NMR spectrum of 2b in benzene-$d_6$ from 8.0 ppm to 5.4 ppm.
The postscripts b and f refer to protons on the bound and free
indole substituents respectively.
To aid assignments of the resonances a 2-D gCOSY experiment was performed. A portion of the spectrum in the aromatic region is shown in Figure 3.5. From the cross peaks in the spectrum we establish the connectivity of the indole portion in the order 8.00 ppm – 7.39 ppm – 7.30 ppm – 7.71 ppm and 7.47 ppm – 7.09 ppm – 6.96 ppm – 6.78 ppm. We notice that each of these series has two doublets and two triplets as expected. The resonance at 8.00 ppm is assigned to H7 on the bound indolyl moiety. This assignment was made on the basis of the report by Mason and co-workers\(^5\) that the resonance for H7 is typically shifted downfield upon coordination of di- and tri(3-methylindolyl)methanes to main group (B,\(^2\) P,\(^5\) Si,\(^3\) Al\(^1\)) or transition (Ti, Zr)\(^4\) elements.

![gCOSY spectrum](image)

**Figure 3.5.** gCOSY spectrum of 2b in benzene-\(d_6\) from 6.40 ppm to 8.00 ppm. The postscripts b and f refer to protons on the bound and free indole substituents respectively.
It may be noted that for phosphines the magnitude of shift was dependent on the size of the group bound to phosphorus.\textsuperscript{25} Therefore we may assign the resonances on the bound indolyl as 8.00 ppm (H7), 7.39 ppm (H6), 7.30 ppm (H5) and 7.71 ppm (H4). Resonances on the free indole may be assigned as 7.47 ppm (H7), 7.09 ppm (H6), 6.96 ppm (H5) and 6.78 ppm (H4).

The resonances in benzene-\textit{d$_6$} for complexes \textbf{2a}, \textbf{2c}, \textbf{2d} and \textbf{3} in the aromatic region are similar and can be assigned analogously. As stated in the last section, the $^1$H NMR spectrum of \textbf{1} in benzene-\textit{d$_6$} is not well resolved so a good comparison cannot be made, but one thing can be noted that H7 resonance appears at 7.59 ppm. So in the bound indolyl the resonance is shifted downfield. Comparing the H4 resonance in the bound indolyl and free indole we observe that in the bound state the H4 resonance appears substantially downfield.

In chloroform-\textit{d} the aromatic regions of the $^1$H NMR spectra are not very well resolved. For \textbf{2d}, there is a broad singlet at 7.89 ppm that can be attributed to the NH proton. There is a doublet, integrating to one hydrogen at 7.56 ppm which can be assigned to H7 in the bound indolyl. The H7 resonance in \textbf{1} appears at 7.47 ppm. There is a doublet at 7.43 ppm integrating to two hydrogens. Assigning resonances in the same order of chemical shifts as in benzene-\textit{d$_6$} we may attribute this to an overlap of bound indolyl H4 and free indole H7. There is a triplet at 7.11 ppm that may be attributed to bound indolyl H6 and a multiplet from 7.03 – 7.01 ppm integrating to 4H attributed to an overlap of bound indolyl H5 and free indole H6, H5 and H4. The imidazolyl H4 and H5 resonances appear at 7.00 ppm and 6.63 ppm and can be distinguished from the coupling
constant $^{3}J_{HH} = 1.8$ Hz. To verify the assignments for the free indole and bound indolyls in chloroform-$d$, a gCOSY experiment was performed on $2c$ in chloroform-$d$. The chemical shifts in this region are similar to those for $2b$ except that the resonance for the imidazolyl H4 overlaps with the bound H6. In the gCOSY spectrum there is a cross peak between the resonance at 7.56 ppm and that at 7.11 ppm indicating that the resonance at 7.11 ppm is bound indolyl H6 (overlapping with imidazolyl H4). The resonance at 7.11 ppm has a cross peak with the multiplet at 7.03–7.01 ppm indicating that the multiplet contains bound indolyl H5. The multiplet at 7.03–7.01 ppm has a cross peak with the resonance at 7.43 ppm indicating that the resonance at 7.43 ppm may contain bound indolyl H4. If we assume that the doublet at 7.43 ppm has free indole H7, then there is only one cross peak between the resonance at 7.43 ppm and the multiplet at 7.03–7.01 ppm, indicating that the multiplet is an overlap of free indole H4, H5, and H6.

Resonances in the aromatic region in chloroform-$d$ for $2a$, $2b$, $2d$ and $3$ can be assigned similarly.

Now, we turn our attention to the aliphatic region. The alkyl substituents on the metal for $2a$, $2b$, $2c$, $2d$ and $3$ are all different, therefore the only resonances that are similar for all the complexes in this region are the methyl resonances for the imidazolyl, the bound indolyl and the free indole. This region of the $^{1}$H NMR spectra had good resolution in both chloroform-$d$ and benzene-$d_{6}$, though comparatively the former affords better resolution. Therefore this region of the spectra is discussed in chloroform-$d$. The assignments in benzene-$d_{6}$ can be made similarly. The imidazolyl methyl resonances for the complexes in chloroform-$d$ appear in the range of 3.47–3.69 ppm. The imidazolyl methyl resonance in $1$ appears at 3.69 ppm. The general trend upon coordination is
upfield shift by about 0.1–0.2 ppm. The methyl resonances for the bound indolyl appear in the range 2.41–2.54 ppm. The resonance for the indolyl methyl in 1 appears at 2.39 ppm. Thus it may be generalized that on complexation this resonance shifts downfield by about 0.1 ppm. This is consistent with the observation of these resonances in the range 2.43 – 2.44 ppm by Fneich\textsuperscript{1} for 5a-d where both the indolyl arms are bound to the central metal. For the free indole arm, the methyl resonance appears in the range 2.24 – 2.28 ppm. Thus it may be generalized that on formation of bidentate complexes the resonance for the methyl on the free indole shifts upfield by 0.1 ppm.

The 600 MHz \textsuperscript{1}H NMR spectrum of 2a has two singlets at −0.39 ppm and −0.52 ppm for the two chemically inequivalent methyls on the aluminum. For 2b, there are two triplets at 1.23 ppm and 0.82 ppm corresponding to the two chemically inequivalent methyls of ethyl groups on aluminum. The methylene protons on each of the ethyls are diastereotopic. Thus, protons on each ethyl group exhibit an ABX\textsubscript{3} type splitting pattern. The set of diastereotopic methylene protons on one of the ethyl appears as a quartet at 0.141 ppm with a coupling constant of $3J_{HH} = 7.8$ Hz. The observation of a quartet indicates that the difference in chemical shifts of the methylene protons must be almost zero. But the diastereotopic methylene protons on the other ethyl appear as two double quartets whose chemical shifts were manually calculated at 0.322 ppm and 0.260 ppm. Each of these integrates to one hydrogen. The $3J_{HH}$ was calculated to be 8.4 Hz and the $2J_{HH}$ was calculated to be 14.4 Hz. To verify our calculations, the splitting pattern was simulated on a simulation software (Figure 3.6).\textsuperscript{26} The simulated pattern matches quite well with the observed pattern, the slight difference being attributed to line broadening in the experimental pattern.
Figure 3.6. Actual (left) and simulated (right) portions of $^1$H NMR (600 MHz, CDCl$_3$) spectrum showing one set of diastereotopic methylene protons in 2b.

For 2c the protons on the two diastereotopic methyl groups on each of the two isobutyl groups appear as doublets. Thus we observe four doublets, each integrating to three hydrogens. The resonances for the methyl protons on one isobutyl appear at 1.03 ppm and 1.02 ppm while the resonances for the methyl protons on the other isobutyl appear at 0.62 ppm and 0.61 ppm. The two methines, one on each of the isobutyls appear as multiplets at 2.05 ppm and 1.54 ppm, each integrating to one hydrogen. The methylene protons on each of the isobutyls are diastereotopic. They appear as two ABX patterns on a 400 MHz spectrometer. The coupling constants and the chemical shifts were manually calculated from the spectra by the procedure described in Bassler and Silverstein,\textsuperscript{23} and simulated on NMR simulating software to verify the correctness. The two-bond coupling constant for one set of diastereotopic protons is substantially more than the coupling constant for the other set. This is consistent with a large difference in chemical
one set of protons appear as well resolved doublet of doublets while the other set appears
as a more complex overlapping doublet of doublets. The chemical shifts for one set of
diastereotopic protons were calculated to be 0.43 ppm and 0.21 ppm. The calculated $^3J_{HH}$
was 7.2 Hz for one proton and 6.8 Hz for the other one. The $^2J_{HH}$ was 14.4 Hz for each
case. For the other set of diastereotopic protons, the chemical shifts are 0.35 ppm and
0.31 ppm. The simulated spectra are shown in Figure 3.7

For complexes 2d and 3 there are two resonances each integrating to nine
hydrogens for the two nonequivalent tert-butyl groups. For 2d they appear at 1.33 ppm
and 0.58 ppm, for 3 they appear at 1.44 ppm and 0.63 ppm.

In the $^{13}$C NMR spectra for 2a-d and 3 there was sufficient resolution in both
benzene-$d_6$ as well as in chloroform-$d$. Complexes 2a-d and 3 all had similar chemical
shifts for corresponding carbons, therefore the discussion on one permits analogous
treatment of the others. We shall discuss 2b here as it has been characterized in detail by
2D NMR spectroscopy.

In the aromatic region of the $^{13}$C NMR spectrum of 2b in chloroform-$d$ the
aromatic region the resonance for the imidazolyl C2 carbon appears at 148.40 ppm. This
is assigned based on that reported by Breitmaier$^{22}$ and coworkers. The secondary and the
tertiary carbons were assigned by observing the chemical shifts in 1 as well as the
tridentate complexes 5a-d synthesized by Fneich.$^1$ In general, the chemical shifts of the
Figure 3.7. Actual and simulated portions of the $^1$H NMR spectrum at 400 MHz in CDCl$_3$ of the diastereotopic methylene protons in 2c (a) two doublet of doublets simulated using $\delta$ 0.432 ($^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 6.8$ Hz), 0.215 ($^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 7.2$ Hz) (b) two doublet of doublets simulated using $\delta$ 0.348 ($^2J_{HH} = 4.8$ Hz, $^3J_{HH} = 6.8$ Hz), 0.312 ($^2J_{HH} = 4.8$ Hz, $^3J_{HH} = 6.8$ Hz) (c) Actual spectrum.
carbons on the free indole arms were similar to the corresponding resonances in 1 and those on the bound indolyl arms were similar to those of the tridentate complexes. For the benefit of the reader these observations are summarized in Tables 3.3 and 3.4.

The assignments were confirmed on the basis of cross peaks observed in the HMQC (Figure 3.8) and HMBC spectra. As an example in Figure 3.8, we notice that the $^{13}$C resonance at 113.55 ppm has a cross peak with the $^1$H resonance at 7.89 ppm that corresponds to the H7 on the bound indolyl. The other $^{13}$C resonances can be similarly assigned.

Figure 3.8. HMQC spectrum of 2b in chloroform-$d$ from 110 to 128 ppm.
From Tables 3.3 and 3.4 it is obvious that all the $^{13}$C resonances except C5 and C6 follow the pattern described earlier. Further studies are necessary to explain this behavior.
The $^{13}$C NMR spectra in the aliphatic region are observed as expected, though the methine CH and the imidazolyl methyl resonances are particularly noteworthy. The resonance for the imidazolyl methyl appears downfield of the methine carbon resonance. This was determined by HMQC (Figure 3.9) and confirmed by HMBC. In the HMQC spectrum of $2b$ in CDCl$_3$, we observe that the $^{13}$C resonance at 33.74 ppm has a cross peak with the $^1$H resonance at 3.35 ppm that corresponds to the imidazolyl methyl group.

The $^{13}$C resonance at 32.41 ppm has a cross peak with the $^1$H resonance at 5.94 ppm that corresponds to the methine proton. There are two resonances in each spectrum for the bound indolyl methyl carbon and the free indole methyl carbon respectively, the former being shifted downfield by 0.1 ppm to 0.8 ppm for the series.

**Figure 3.9.** A portion of the HMQC spectrum in CDCl$_3$ for $2b$ from 110 ppm to 30 ppm
Complexes 2d and 3 were also characterized by X-ray crystallography. The ORTEP diagram of 2d is shown in Figure 3.10 while that of 3 is shown in Figure 3.11. The summary of selected bond distances and angles for the structures of 2d and 3 are shown in Tables 3.5 and 3.6, respectively.

The solution of the crystal structure of 2d confirms our inference from the NMR data. One indolyl arm of 1 is deprotonated and bound to aluminum and the other indole arm is free. The imidazolyl coordinates to the metal forming a six-membered ring thus providing additional stability to the system. The Al–N_{imidazolyl} bond length for complex 2d is 1.9496(15) Å. The length of the Al–N_{pyridyl} bond in 5b\textsuperscript{1} is 1.980(5) Å. In the bidentate complex 6 of di(3-methylindolyl)pyridyl methane ligand with tri-tertbutylaluminum, as discussed in chapter 2, the Al–N_{pyridyl} distance is 2.009(2) Å, while in the bimetallic complex 8a (see chapter 2) of the same ligand with trimethylaluminum the Al–N_{pyridyl} distance is 1.968(2) Å. Thus it may be inferred that the M–N_{pyridyl} distance is comparable in all the above similar complexes. The unit cell parameters, space group, bond distances and angles for complexes 3 and 2d are very similar. The Ga atom has a larger radius (0.63 Å) than the Al atom (0.50 Å)\textsuperscript{27} this accounts for the slight difference in data for these complexes. Molecules of 2d and 3 are isomorphic.
Figure 3.10. ORTEP diagram of 2d. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, except the indole NH, are omitted for clarity.

Table 3.5. Selected bond distances and angles for 2d

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Figure 3.11. ORTEP diagram of 3. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, except the indole NH, are omitted for clarity.

Table 3.6. Selected bond distances and angles for 3

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<td>C11–N1–Ga</td>
<td>124.2(2)</td>
<td></td>
</tr>
<tr>
<td>N1–Ga–N3</td>
<td>91.98(6)</td>
<td></td>
</tr>
<tr>
<td>Ga–N3–C2</td>
<td>126.7(2)</td>
<td></td>
</tr>
<tr>
<td>N3–C2–C1</td>
<td>126.7(3)</td>
<td></td>
</tr>
<tr>
<td>C2–C1–C11</td>
<td>115.0(14)</td>
<td></td>
</tr>
<tr>
<td>C1–C11–N1</td>
<td>121.7(3)</td>
<td></td>
</tr>
<tr>
<td>N2–C21–C1</td>
<td>119.9(3)</td>
<td></td>
</tr>
</tbody>
</table>
For the bound indolyl arm the $\text{M} - \text{N}_\text{indolyl}$ distance is 1.9070(14) Å for 2d and 1.976(3) Å for 3. In 5b the $\text{Al} - \text{N}_\text{indolyl}$ distances are 1.845(6) Å and 1.870(6) Å respectively for the two bound indolyl arms. In 6 the $\text{Al} - \text{N}_\text{indolyl}$ distance for the bound indolyl is 1.884(2) Å, while in 8a the corresponding distance is 1.885(2) Å. Cowley and coworkers reported $\text{Al} - \text{N}_\text{pyrrolyl}$ bond lengths in the range 1.824–1.827 Å (the average being 1.825 Å) for (pyrrolyl)$_3$(Me$_3$NH)Al. Thus this length is also comparable to corresponding lengths in similar complexes. This length is much shorter than the length of 2.022 Å for bond of Al with the N of the bridging indole in 8a. The larger value for 3 may again be attributed to the larger radius of Ga.

The interior angles in the six-membered ring $\text{C}_3\text{N}_3\text{M}$ are all close to 120° except the angle $\text{N}_1$$\text{M}$$\text{N}_3$ which are 94.28° for 2d and 91.98° for 3. For 5b, the corresponding angle is 99.6° and for 6 it is 95.06°. We now look at the angles around the three nitrogens capable of chelating to the central metal. If the sum of the three angles subtended by an atom with its three neighboring atoms is to 360° then that atom is planar. For 2d, the sum of the three angles subtended by N1 and N3 with their respective neighboring atoms are

<table>
<thead>
<tr>
<th>Complex</th>
<th>M</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Al</td>
<td>tBu</td>
</tr>
<tr>
<td>7</td>
<td>Ga</td>
<td>tBu</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>8a</td>
<td>Me</td>
</tr>
<tr>
<td>8b</td>
<td>Et</td>
</tr>
</tbody>
</table>
352.46° and 358.61°. This implies that N1 lies essentially in the plane of the six-membered ring C₃N₃Al. The corresponding values for 3 are 351.0° and 358.3°. Similar conclusions can be drawn for this complex too.

3.3.3 Preparation and characterization of bimetallic complexes 4a and 4b.

It was observed that stoichiometry is important for the reaction of 1 with AlR₃ (R = Me, Et) since use of more than one equivalent of the aluminum alkyl results in formation of bimetallic complexes analogous to 8a and 8b reported for the di(3-methylindolyl)pyridylmethane ligand (see chapter 2). Reaction of two equivalents of trimethylaluminum with one equivalent of 1 in toluene results in the formation of a yellow bimetallic complex (eq 4).

\[
\begin{align*}
\text{H₃C} & \quad \text{H₃C} \\
\text{H₃C} & \quad \text{H₃C} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{H₃C} & \quad \text{H₃C} \\
\end{align*}
\]

\[+ 2 \text{AlR₃} \rightarrow \text{toluene} \quad 2 \text{h, } 20 \degree \text{C} \rightarrow \]

\[\begin{align*}
\text{H₃C} & \quad \text{H₃C} \\
\text{H₃C} & \quad \text{H₃C} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\text{H₃C} & \quad \text{H₃C} \\
\end{align*}
\]

\[+ 2 \text{RH} \quad \text{(4)}
\]

<table>
<thead>
<tr>
<th>Complex</th>
<th>M</th>
<th>R</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>Al</td>
<td>Me</td>
<td>66%</td>
</tr>
<tr>
<td>4b</td>
<td>Al</td>
<td>Et</td>
<td>44%</td>
</tr>
</tbody>
</table>

The \(^1\)H NMR spectrum of 4a in chloroform-\(d\) has four resonances at −1.94 ppm, −1.51 ppm, −0.58 ppm and −0.28 ppm each integrating to three with respect to the single methine peak at 5.94 ppm indicating that there are four nonequivalent methyl groups
attached to aluminum. The methyl resonances are shifted upfield compared to the corresponding resonances in free trimethylaluminum. There are two resonances at 2.57 ppm and 2.31 ppm each integrating to three corresponding to two indolyl methyl resonances indicating that the two indolyl arms of the complex are nonequivalent. The resonance for the indolyl methyl in 1 appears at 2.39 ppm, while the resonances for protons on the the free indole and the bound indolyl methyls in 2a appear at 2.28 ppm and 2.41 ppm respectively. Thus we may infer that the chemical environment around one of the indolyl methyls is similar to the bound indolyl methyl, while the other is different from the free indole methyl in 2a. The resonance for the imidazolyl methyl appears at 3.68 ppm. The corresponding values for 1 and 2b are 3.69 ppm and 3.47 ppm. In the aromatic region there are two distinct sets of resonances for the two indolyl arms indicating that they are under different chemical environments. There is one resonance for the methine proton, indicating the formation of a single species. There is no broad resonance around 9.0 ppm, corresponding to the indole NH, indicating that both the indole substituents have been deprotonated.

A similar complex of di-(3methylindolyl)pyridylmethane with trimethylaluminum 8a was synthesized by Fneich, though he proposed the structure to be a methyl bridging bimetallic complex based on 1D and 2D NMR spectroscopy. Later it was elucidated by means of X-ray crystallography that the two aluminums are bridged by an N-bound 3-methyldindolyl group of the ligand as discussed in chapter 2. The ethyl analog of the complex was also synthesized and characterized by NMR spectroscopy.

Based on the crystallographic characterization of Fneich’s complex and observing the similarity of the two ligands it is proposed that the two aluminums alkyls are bridged
by an indolyl nitrogen. One of the aluminum s is coordinated by indolyl nitrogen, while the other is coordinated to a imidazolyl nitrogen.

The ethyl analog \(4b\) was synthesized and characterized by \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy. The spectral characteristics in the aromatic region of the \(^1\text{H}\) spectra of \(4b\) are similar to \(4a\), hence will not be discussed here. The aliphatic region of the \(^1\text{H}\) NMR spectrum, shown in Figure 3.12, displays interesting features. The eight methylene protons, two each on the four ethyls, are diastereotopic. They appear as eight distinct multiplets each integrating to one hydrogen. The methyls on each of the four ethyls appear as four triplets each integrating to three hydrogens.

Figure 3.12. Aliphatic region of the \(^1\text{H}\) NMR spectrum of \(4b\) in chloroform-\(d\) from 4.0 ppm to \(-2.0\) ppm

The \(^{13}\text{C}\) NMR spectrum of \(4a\) and \(4b\) are similar. For \(4a\), there are four broad resonances upfield of TMS for the four methyl carbons on aluminum. For \(4b\), two of them are upfield of TMS and two downfield. Additionally the spectrum for \(4b\) has four resonances for methylene carbons. For both \(4a\) and \(4b\) there are two resonances each for
the two inequivalent indolyl methyl carbons, one resonance for the imidazolyl carbon and one for the methine carbon.

The assignment of the resonances in the aromatic region was aided by HMBC and HMQC experiments. The overlap of $^1$H NMR resonances in the aromatic region of the spectra makes the assignment difficult. Hence the inference from the correlation experiments is tentative and further studies are required to verify the assignments made here. A noteworthy feature is that the bridging C3 indolyl resonance is shifted downfield by approximately 15 ppm to 120.68 ppm for $4a$ and 122.03 ppm for $4b$.

There are complexes of main group elements bridged by indoles. Weiss$^{29}$ and coworkers synthesized lithioindole and sodioindole complexes and characterized them by NMR spectroscopy and X-ray crystallography. The lithioindole dimers were found to exist in syn and anti configurations in solution. Other examples of indolyl moieties bridging main group metals are discussed in chapter 1.

Solutions of $4a$ in benzene-$d_6$, chloroform-$d$ and toluene are visually fluorescent. Future work may include quantifying the fluorescence of this complex.

3.3.4 Attempts to synthesize the tridentate complexes

To achieve coordination of the free indole arm in complexes $2a-d$ and $3$ two procedures were attempted. In the first procedure, one equivalent of $2d$ was reacted with one equivalent of tri-$tert$-butylaluminum in toluene under reflux for 20 h. But starting material was obtained even after 24 h reflux. In the second procedure one equivalent of $1$ was deprotonated using two equivalents of $^n$BuLi in THF as solvent. This was followed by reaction with one equivalent of $^1$BuAlCl$_2$ in an attempt to synthesize $^1$BuAl(1-CH$_3$-2-
C<sub>3</sub>H<sub>2</sub>N<sub>2</sub>)HC(3-CH<sub>2</sub>C<sub>8</sub>H<sub>4</sub>N)<sub>2</sub>. This resulted in the formation of a green solid, which could not be identified by NMR spectroscopy. It may be noted though that just preliminary investigations were carried out for achieving synthesis of tridentate complexes by this route. Further studies are required in this direction.

The tendency of 1 to form bidentate complexes as opposed to tridentate ones formed by the di(3-methylindolyl)pyridylmethane ligand<sup>1</sup> may be attributed to the difference in basicity of the imidazolyl and the pyridyl arms in the respective ligands.

### 3.4 Conclusions

A series of bidentate complexes of di(3-methylindolyl)imidazolylmethane (1) with trimethylaluminum, triethylaluminum, tri-iso-butylaluminum, tri-tert-butylaluminum and tri-tert-butylgallium 2a–d and 3, respectively, have been synthesized. Two bimetallic complexes of 1 with trimethylaluminum and triethylaluminum 4a and 4b have also been synthesized. All complexes were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The complexes 2d and 3 were characterized by X-ray crystallography. The structures of 4a and 4b are proposed to be bimetallic with the two aluminum atoms bridged by an N-bound 3-methylindolyl group.
3.5 References

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