



Synthesis and structural aspects of gallium compounds containing tridentate pincer type pyrrolyl ligands: Intramolecular hydrogen bonding of gallium aryloxides



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ABSTRACT

A series of gallium derivatives incorporating with pincer type tridentate symmetric and asymmetric pyrrolyl ligands are conveniently synthesized. Compilation of a symmetrical tridentate pyrrole ligand, $[C_4H_2NH-(2,5-CH_2NH^tBu)_2]$ (**1**) with one equiv of *n*-BuLi in heptane generates lithiated **1** that turns to Ga $[C_4H_2N-(2,5-CH_2NH^tBu)_2]Cl_2$ (**2**) subjecting the addition of GaCl₃/ether suspension into diethyl ether. Reacting **2** with two equiv of lithium reagents (LiR) in same solvent originates a series of gallium compounds Ga $[C_4H_2N-(2,5-CH_2NH^tBu)_2]R_2$ (**3**, R = Me; **4**, R = O-C₆H₄-4-Me; **5**, R = O-C₆H₃-2,6-Me₂) in moderate yield through metathesis reactions. Furthermore, the combination of a tridentate asymmetrical pyrrole ligand, $[C_4H_2NH(2-CH_2NH^tBu)(5-CH_2NMe_2)]$ and *n*-BuLi initiates the lithiated **6** that undergoes the formation of a penta-coordinated gallium compound GaCl₂ $[C_4H_2N(2-CH_2NH^tBu)(5-CH_2NMe_2)]$ (**7**) while reacting with GaCl₃. Furthermore, reacting **7** with two equivs of MeLi affords the gallium-alkyl compound, GaMe₂ $[C_4H_2N(2-CH_2NH^tBu)(5-CH_2NMe_2)]$ (**8**) in high yield. The Ga-derivatives are characterized by ¹H and ¹³C NMR spectroscopy and the molecular structures of **2**, **3**, **4**, **5** and **7** are determined by single crystal X-ray diffractometry in solid state.

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1. Introduction

Gallium compounds containing nitrogen-donor tridentate ligands were studied and used in various applications in past decades [1–3]. These gallium compounds can be used as catalysts for ring opening polymerization [4–7] and olefin polymerization [8–11], metal-based drugs [12–17] and as precursor for chemical vapor deposition [18–22]. The NNN tridentate ligands, coupled in gallium entity are shown in Scheme 1 where (a) and (b) act as neutral ligands and (c)–(g) function as mono anionic ligands [23–31]. Considering different ligand moieties, pyrrolyl system is well capable to bring metal atoms into close proximity and furnishes an intramolecular or intermolecular pathway for bonding interactions. In whatever manner, relatively few metal-pyrrole compounds have been found to be synthetically useful with substituted pyrrole based architecture. In our previous articles, we have employed bi- or tri-dentate, substituted pyrrolyl ligands $[C_4H_3N$

$\{2,5-(CH_2NMe_2)_2\}]$ [32,33] as auxiliary ligands with early transition metals [34–36] or group 13 metals [37,38] to form organometallic compounds, and we assessed their reactivity toward small organic molecules.

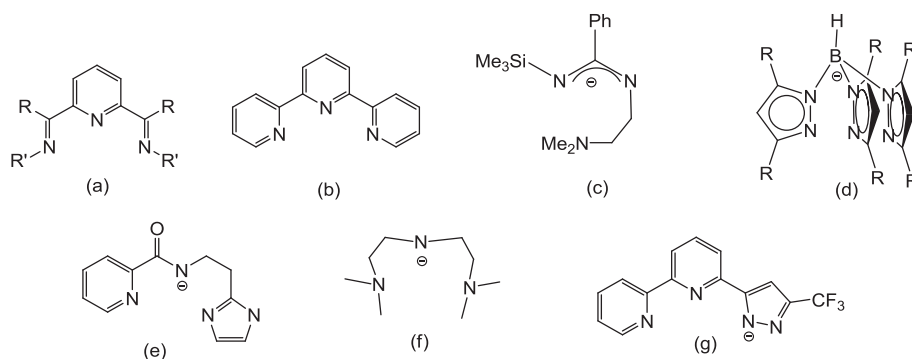
As an extension of our prolonged interest in the pyrrolyl mediated precursors, the current contribution focuses the synthesis and characterizations of a series of gallium compounds containing NNN symmetric and asymmetric tridentate ligands (Schemes 2 and 3).

2. Results and discussion

2.1. Synthesis and characterization

A series of gallium compounds containing tridentate pincer type symmetric and asymmetric pyrrole ligands, $[C_4H_2NH-(2,5-CH_2NH^tBu)_2]$ and $[C_4H_2NH(2-CH_2NH^tBu)(5-CH_2NMe_2)]$, were synthesized and characterized by NMR spectroscopy and single crystal X-ray diffractometry. Reacting $[C_4H_2NH-(2,5-CH_2NH^tBu)_2]$ (**1**) with one equiv of *n*-BuLi in heptane generates lithiated **1** that undergoes

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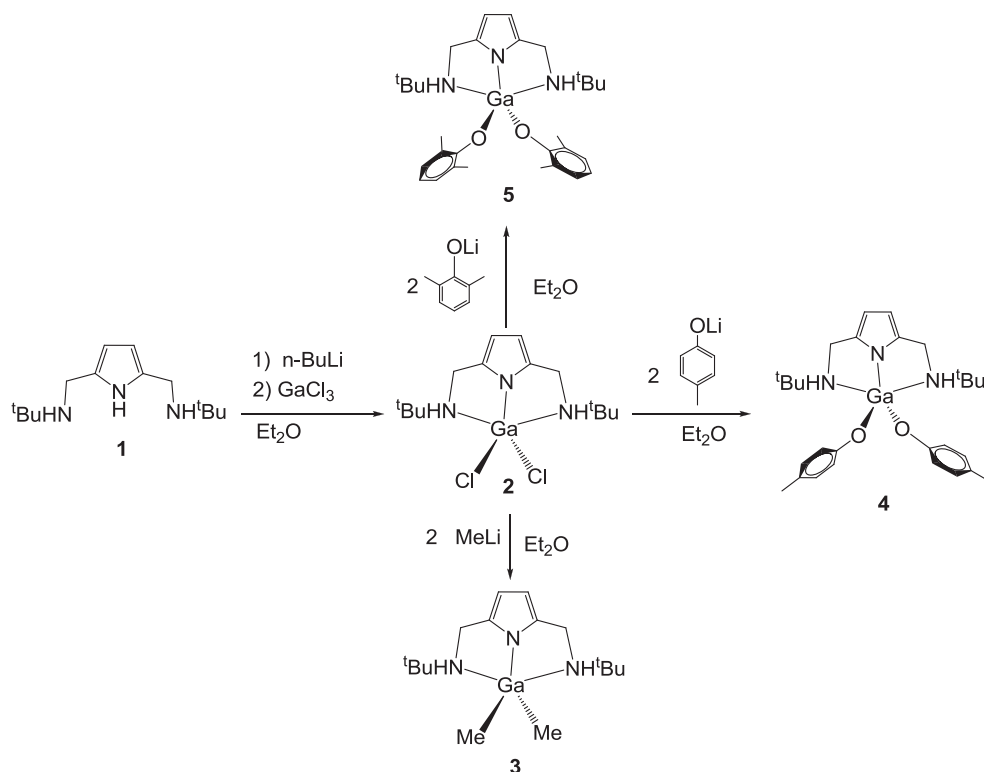
Scheme 1. NNN tridentate ligands used in gallium compounds.

with GaCl_3 /ether suspension in diethyl ether to yield $\text{Ga}[\text{C}_4\text{H}_2\text{N}-(2,5\text{-CH}_2\text{NH}^t\text{Bu})_2]\text{Cl}_2$ (**2**) in 75% yield. Compound **2** shows one distinct doublet at δ 3.45 in the ^1H NMR spectrum representing the methylene protons of the $\text{CH}_2\text{NH}^t\text{Bu}$ fragment [39–41]. The doublet is raised by the $^3J_{\text{HH}}$ coupling of corresponding methylene and amine proton.

Reacting **2** with two equivs of lithium reagents (LiR) in diethyl ether initiates a series of gallium compounds $\text{Ga}[\text{C}_4\text{H}_2\text{N}-(2,5\text{-CH}_2\text{NH}^t\text{Bu})_2]\text{R}_2$ (**3**, $\text{R} = \text{Me}$; **4**, $\text{R} = \text{O}-\text{C}_6\text{H}_4-4\text{-Me}$; **5**, $\text{R} = \text{O}-\text{C}_6\text{H}_3-2,6\text{-Me}_2$) in moderate yield through metathesis pathways. The methylene protons of $\text{CH}_2\text{NH}^t\text{Bu}$ fragments of **3–5** show similar ^1H NMR chemical shift in the range of δ 3.67–3.59. It is noticed that the chemical shift of amino proton of $\text{CH}_2\text{NH}^t\text{Bu}$ fragment in **3–5**, they belong at δ 2.10, 1.03, and 2.50, respectively. Among these, compounds **3** and **5** show quite similarity with **2**, however, **4** remains in more up-field region than previous ones. This phenomenon can be described as the consequence of less steric congestion in **4**, facing an

intra-molecular hydrogen bonding, $^t\text{BuNH}\dots\text{O}-\text{C}_6\text{H}_4-4\text{-Me}$ [42]. Nevertheless, the bulky $\text{O}-\text{C}_6\text{H}_3-2,6\text{-Me}_2$ group in **5** prohibits the hydrogen bonding as $^t\text{BuNH}\dots\text{O}-\text{C}_6\text{H}_3-2,6\text{-Me}_2$.

Similarly, when the tridentate asymmetrical pyrrole ligand $[\text{C}_4\text{H}_2\text{NH}(2\text{-CH}_2\text{NH}^t\text{Bu})(5\text{-CH}_2\text{NMe}_2)]$ is compiled with $n\text{-BuLi}$ and GaCl_3 , a five-coordinated gallium compound $\text{GaCl}_2[\text{C}_4\text{H}_2\text{N}(2\text{-CH}_2\text{NH}^t\text{Bu})(5\text{-CH}_2\text{NMe}_2)]$ (**7**) forms in moderate yield. Furthermore, the condensation between **7** and two equivs of MeLi affords gallium-methyl compound, $\text{GaMe}_2[\text{C}_4\text{H}_2\text{N}(2\text{-CH}_2\text{NH}^t\text{Bu})(5\text{-CH}_2\text{NMe}_2)]$ (**8**) in high yield. ^1H NMR spectrum of **7** in CDCl_3 shows one singlet and one doublet at δ 3.63 and 3.90 for corresponding methylene protons of CH_2NMe_2 and $\text{CH}_2\text{NH}^t\text{Bu}$ fragments, respectively. The amino proton of NH^tBu appears at δ 2.32, quite similar with **2**, **3**, and **5**. In compound **8**, the chemical shift of corresponding methyl fragments of GaMe_2 appears at -0.28 and -6.6 , respectively for its ^1H and ^{13}C NMR resonances.



Scheme 2. Synthesis of compounds **1–5**.

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