行政院國家科學委員會專題研究計畫成果報告

計畫編號：NSC 90-2113-M-018-003
執行期限：90 年 8 月 1 日至 91 年 7 月 31 日

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一、中文摘要

$GaCl_3$ 與 $Li[NC_4H_3(CH_2NMe_2)$-2] (n = 1, 2, 3) 於乙醚中並在 –78 °C 下反應產生 $GaCl_{3-n}[NC_4H_3(CH_2NMe_2)-2]_n$ (n=1, **1**; n=2, **2**; n=3, **3**)。 化合物 **1** 與兩當量之 RLi 反應，經由金屬交換反應而產生 $GaR_2[NC_4H_3(CH_2NMe_2)$-2] (**4a**, **R=Me**; **4b**, **R=Bu**)。 當 **2** 與一當量之 RLi 於乙醚中反應, **3** 和 **4** 會經由配位基的交換而產生。. 由變溫 ^{1}H NMR 光譜實驗得知，五配位之 化合物 **3** 於溶液中會進行轉換而在 5 °C 時會得到合併點。其 $\Delta G^{\neq}$ 約爲 10.4 Kcal/mole. 首有之化合物均經由 ^{1}H 和 ^{13}C NMR 光譜鑑定。 化合物 **3** 和 **4a** 亦經由 X 光繞射一件定期結構。

關鍵詞：砒各、轉換

Abstract

Treatment of $GaCl_3$ with $Li[NC_4H_3(CH_2NMe_2)$-2] (n = 1, 2, 3) in diethyl ether at –78 °C yields $GaCl_{3-n}[NC_4H_3(CH_2NMe_2)-2]_n$ (n=1, **1**; n=2, **2**; n=3, **3**). Compound **1** reacts with two equiv of RLi to afford $GaR_2[NC_4H_3(CH_2NMe_2)$-2] (**4a**, **R=Me**; **4b**, **R=Bu**) via transmetallation. Reacting **2** with one equiv of RLi in diethyl ether, **3** and **4** are formed via ligand redistribution. Variable temperature ^{1}H NMR spectroscopic experiments reveal that the five-coordinate gallium compound **3** is fluxional and results in a coalescence temperature at 5 °C, at which $\Delta G^{\neq}$ is calculated at ca. 10.4 Kcal/mole. All the new compounds have been characterized by ^{1}H and ^{13}C NMR spectroscopy and the structures of compounds **3** and **4a** have also been determined by X-ray crystallography.

Keywords: gallium, pyrrole, fluxional

二、Introduction

Metallocene chemistry has been a blooming topic in the past two decades and most of the ligands focused on are Cp related, and the metals involved are high oxidation state early transition metals.[1] However, more research groups have turned their attention to non-Cp ligands, such as alkoxide,[2] amide,[3] carbamate,[4] etc. and have extended metals to group 13 and late transition metals. Some gallium complexes containing multidentate non-η^5-Cp type ligands have been synthesized and structurally characterized.[5-7] We have been interested in the preparation of early transition metals,[8] or group 13 metal,[9] complexes supported by bi or tridentate substituted pyrrole ligands, and their reactivity toward small organic molecules. Herein we report the synthesis and characterization of gallium complexes bearing bi-dentate substituted pyrrolyl ligand.

三、Results and Discussion

Synthesis and characterization. The reactions of $GaCl_3$ with $Li[NC_4H_3(CH_2NMe_2)$-2] resulted in alkylation and ligand redistribution reactions which are summarized in Scheme 1.

Scheme 1 here

The reaction of $GaCl_3$ with one equiv $Li[NC_4H_3(CH_2NMe_2)$-2] in diethyl ether at –78 °C yields the bidentate pyrrolyl gallium dichloride compound $GaCl_2[NC_4H_3(CH_2NMe_2)$-2] (**1**). Compound **1** was isolated as a dark red solid by removal of the volatiles after prolonged

vacuum drying. ^{1}H and ^{13}C NMR spectra of **1** are consistent with the structure of a psuedo-C_s symmetry, in which the mirror plane bisects the Cl–Ga–Cl plane and contains the N(pyrrolyl)–Ga–N(amine) plane. Two resonances of ^{1}H and ^{13}C NMR spectra, characteristic of methylene and N-methyl units of $[NC_4H_3(CH_2NMe_2)\text{-}2]$ of compound **1** are observed (see Table 1).

Similarly, the reaction of $GaCl_3$ with two equiv of $Li[NC_4H_3(CH_2NMe_2)\text{-}2]$ in diethyl ether at –78 °C affords $GaCl[NC_4H_3(CH_2NMe_2)\text{-}2]_2$ (**2**) in 94% yield. Again, the ^{1}H NMR spectrum of **2** reveals two singlets associated with the CH_2 and NMe_2 unit of $[NC_4H_3(CH_2NMe_2)\text{-}2]$, indicating a symmetrical structure.

The reaction of $GaCl_3$ with three equiv of $Li[NC_4H_3(CH_2NMe_2)\text{-}2]$ in diethyl ether at –78 °C yields *tris*-bidentate substituted pyrrolyl gallium compound $Ga[NC_4H_3(CH_2NMe_2)\text{-}2]_3$ (**3**) in good yield (Scheme 1). ^{1}H NMR spectrum of **3** at room temperature exhibits one set resonance of $[NC_4H_3(CH_2NMe_2)\text{-}2]$, which either resulted from magnetic equivalent of substituted pyrrole ligands or via fast exchanging and will be discussed later.

Methylation of compound **1** with two equiv of RLi (R= Me or Bu) in diethyl ether at -78 °C affords dialkyl gallium compound $GaR_2[NC_4H_3(CH_2NMe_2)\text{-}2]$ (**4a**, R=Me; **4b**, R=Bu). The pale red solid of compound **4a** could be isolated in high yield by removal of volatiles after filtration and colorless crystals were obtained via vacuum sublimation. The pink color may result from a small amount of unidentified compound. However, compound **4b** was isolated as yellow liquid after filtration and removal of volatiles. The ^{1}H NMR data show that the gallium attached methyl groups of **4a** appeared at δ – 0.26 while the butyl group of **4b** appeared at δ 1.29, 0.88, and 0.49.

Attempts to alkylate compound **2** with one equiv of RLi (R=Me or Bu) in diethyl ether at –78 °C afforded compounds **3** and **4**, which were isolated and characterized by NMR spectroscopies. Ligand redistribution has been attributed to the formation of both products with the common intermediate, $GaR[NC_4H_3(CH_2NMe_2)\text{-}2]_2$ for the reactions.

X-ray crystallographic analysis of $Ga[NC_4H_3(CH_2NMe_2)\text{-}2]_3$ 3 and $GaMe_2[NC_4H_3(CH_2NMe_2)\text{-}2]$ 4a. Colorless crystals of **3**, suitable for X-ray crystallographic analysis, were obtained from a solid sample of compound **3** at room temperature via slow sublimation. The structure is outlined in Figure 1. The structure of **3** is a distorted trigonal bipyramid in which the gallium atom is surrounded by nitrogen atoms of three pyrrolyl units and of two NMe_2 units. Two of the three substituted pyrrolyl ligands are chelated to gallium while the third binds to gallium solely through the pyrrolyl nitrogen atom leaving one NMe_2 outside the coordination sphere. Two nitrogen atoms of NMe_2 units occupy the axial positions with an N(6)-Ga-N(2) angle of 173.62(10)°. The three nitrogen atoms of the pyrrolyl units construct a trigonal plane with the sum of N(1)-Ga-N(3), N(1)-Ga-N(5), and N(3)-Ga-N(5) at 358.6°. Comparing the bond distances of Ga to nitrogen atoms, it is noted that the bond distance of Ga-pyrrolyl (av. 1.916 Å) is 0.39 Å shorter than that of Ga-NMe_2 (av. 2.306 Å) indicating a stronger σ bonded Ga-pyrrolyl than coordinating bonded Ga-NMe_2. Further, two $[C_4H_3N(CH_2NMe_2)\text{-}2]$ ligands chelate to the gallium atom forming two five member rings with acute binding angles of 77.5(1) and 81.9(1)°.

.Figure 1

Colorless crystals of compound **4a**, suitable for X-ray structure determination, were obtained by sublimation at room temperature under vacuum. X-ray data are outlined in Table 2, and selected bond distances and angles are shown in Table 3. The molecular geometry of **4a** is shown in Figure 2, which can be described as a tetrahedral structure with an acute biting angle of 83.64(11)° at N(1)-Ga-N(2) for $[NC_4H_3(CH_2NMe_2)\text{-}2]$. The bond distance of Ga-pyrrolyl nitrogen (1.941(3) Å) is similar to that of in **3**; however, the bond distance of Ga-NMe_2 (2.117(3) Å) in **4a** is ca. 0.19 Å shorter than that of in **3**. A steric

interaction is attributed as the effect.

Fig. 2 here.

Variable temperature ^{1}H NMR spectroscopy of compound 3. The room temperature ^{1}H NMR spectrum of **3** is intriguing, especially in comparison to the solid-state structure, which has been described in terms of a distorted trigonal bipyramidal with two NMe_2 units arranged in axial positions. A symmetrical structure, with resonances at 3.49 and 2.13 ppm for the CH_2N and NMe_2 units, respectively, were observed in the ^{1}H NMR spectrum in $CDCl_3$ at 20 °C. The dynamic property of compound **3** in solution can be resolved by a variable temperature NMR experiment which was performed in the range of –60 °C to 20 °C (Figure 3). A characteristic feature of the low-temperature ^{1}H NMR spectrum of **3** in $CDCl_3$ (at –60 °C) is the presence of six resonances for the diastereotopic methylene protons. As noted in the description of the solid-state structure, the molecule has C_1 symmetry, and, evidently, this is maintained in solution at low temperature. On warming the $CDCl_3$ solution of compound **3**, we observed a coalescence of *ca.* 228 K for the CH_2N protons, which gives a calculated activation energy of $\Delta G^{\ddagger}$ = 10.4 Kcal/mole. A rapid, intramolecular fluxioality of ligand at higher temperatures may have caused the coalescence.

Figure 3 here

Compounds **4a** and **4b** are found to the subject of addition with phenyl isocyanate, 2,5-pentandione, 2,3-butandione, and propene-oxide, under various conditions. However, bulky unsaturated hydrocarbon or ketone such as norbornene, 9-fluorenone, diphenylacetylene, and benzil, are inert toward compound **4**. Detailed mechanistic studies and characterization of final products are still ongoing.

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Scheme 1.

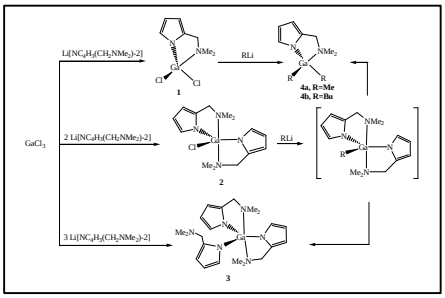


Figure 1.

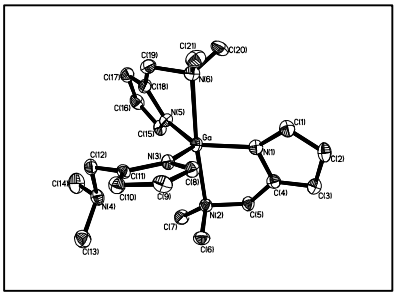


Figure 2.

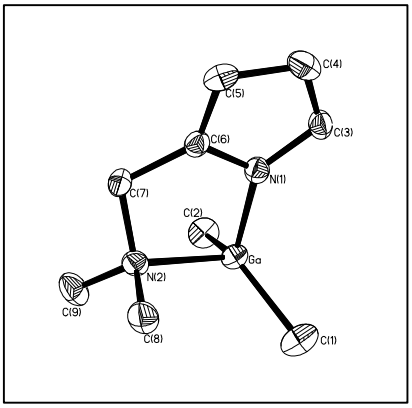
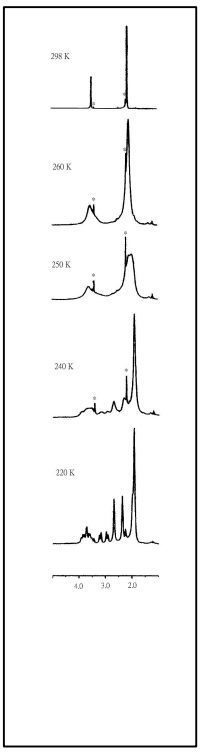


Figure 3.



附件：封面格式

行政院國家科學委員會補助專題研究計畫成果報告

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※　　含具取代之砒各配位基之 13 族化合物的合成、　※

※　　　反應以及聚合反應　　　　　　　　　　　　　※

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計畫類別：□個別型計畫　　□整合型計畫

計畫編號：NSC 90－ 2113 －M－018－003－

執行期間：90 年　08 月　01 日至 91 年　07 月 31　日

計畫主持人：黃瑞賢

共同主持人：

計畫參與人員：

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執行單位：彰化師大化學系

中　華　民　國　91 年　10 月　05 日