

Chemistry of (tetramethylcyclopentadienyl)gallium(III) compounds

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Abstract

Two tetramethylcyclopentadienyl gallium(III) compounds $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ and $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}\cdot\text{pyridine}$ have been prepared and characterized. In contrast, when the syntheses of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$ and $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$ were attempted by metathetical and/or ligand redistribution reactions, the isolated product in each case was a mixture of chemically related compounds rather than single species. When pyridine was added to a solution prepared by combining $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ and GaCl_3 in a 1:2 mol ratio in diethyl ether, the product was the adduct $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}\cdot\text{pyridine}$, a yellow–green crystalline solid. An elemental analysis, ^1H - and ^{13}C -NMR spectra and an X-ray structural study confirmed the identity of this gallium–nitrogen adduct. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Organogallium compounds; Gallium cyclopentadienide derivatives; Tetramethylcyclopentadienide derivatives; X-ray structural study

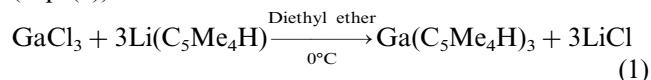
1. Introduction

The factors that permit a heteroleptic organogallium compound with two different organic substituents to exist as a pure compound rather than undergo a ligand redistribution reaction to form a mixture of compounds have been the subject of recent investigations [1–4]. Current research suggests that single compounds exist if the parent molecule is associated and the gallium is four coordinate [1]. However, when monomers are present, multiple species are formed by facile ligand redistribution reactions. Examples of ligands (L) that stabilize heteroleptic organogallium compounds of the type R_2GaL (R = Me, Et) include $\text{C}\equiv\text{CPh}$ [5], C_5H_5 [2,3] and $\text{C}_5\text{H}_4\text{Me}$ [1]. In contrast, ligands such as *t*-butyl [6] and $\text{C}_5\text{H}_4\text{SiMe}_3$ [1] cannot stabilize heteroleptic compounds in the condensed phase or in solution. In order to learn more about the role of steric effects and fluxional processes on the stability of heteroleptic cyclopentadienyl gallium compounds, we wanted to attempt the synthesis of $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$. Previous research suggested that the best route to

$\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$ would be a stoichiometric ligand redistribution reaction [1–3] between $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ [7] and GaMe_3 but a metathetical reaction between $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$ and LiMe might also be successful. When we attempted the preparation and characterization of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ [7] and of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ [7], significant difficulties were encountered. Our characterization data for $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ were inconsistent with the literature. When we attempted the preparation of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$, we obtained a mixture of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$ and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ rather than a pure compound. Thus, the following paper describes the synthesis and characterization of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ and $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}\cdot\text{pyridine}$ as well as the experimental observations that we gathered during our attempted preparations of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$ and $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$.

2. Results and discussion

Our reinvestigation of the synthesis of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ [7] involved the use of a metathetical reaction between GaCl_3 and excess $\text{Li}(\text{C}_5\text{Me}_4\text{H})$ in diethyl ether at 0°C (Eq. (1)).



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The organogallium product was purified by recrystallization from ether and isolated in greater than 70% yield as colorless, thin hexagonal-sheets. The limited solubility of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ in ether required the collection of multiple (9) crops of crystals in order to isolate the product in high yield. The original preparation of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ used an analogous metathetical reaction of GaCl_3 in diethyl ether but the alkylating agent was $\text{Na}(\text{C}_5\text{Me}_4\text{H})$ [7]. The original product was also purified by recrystallization from ether but colorless needles (two crops, 79% yield) were obtained.

Two aspects of the new characterization data suggest that a pure compound has been prepared and isolated. The melting point of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ is sharp but surprisingly high at 225–227.5°C, especially since $\text{Ga}(\text{C}_5\text{Me}_5)_3$ [7,8] melts at 168–170°C to a yellow liquid [8]. The monosubstituted cyclopentadienyl derivatives $\text{Ga}(\text{C}_5\text{H}_4\text{Me})_3$ [1] and $\text{Ga}(\text{C}_5\text{H}_4\text{SiMe}_3)_3$ [1] are mobile liquids at room temperature, whereas $\text{Ga}(\text{C}_5\text{H}_5)_3$ melts with decomposition at 45°C [9]. No melting point was described for the sample originally reported to be $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ [7]. The elemental analyses for the products from the two synthetic procedures are different. The analytical data for the percent carbon and hydrogen of the new compound from the current work are in excellent agreement with the calculated values (Calc. for $\text{C}_{27}\text{H}_{39}\text{Ga}$: C, 74.84; H, 9.07; Found: C, 74.85; H, 9.17%). In contrast, the experimental value for the percent carbon for a sample of the product from the original synthesis was lower than the calculated value by 1.20% but the percent hydrogen was low by only 0.17% (Found: C, 73.64; H, 8.90%) [7].

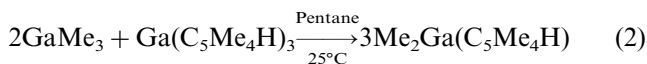
The $^1\text{H-NMR}$ spectra for benzene- d_6 solutions of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ as prepared in the current study and in the original work [7] are different. The spectrum in the current study exhibited only two resonances with relative integrations of 1:12 and thus was unexpected. The less intense resonance at 3.22 ppm may be assigned to the lone ring proton, whereas an intense resonance at 1.95 ppm is due to the protons of the four methyl groups. The spectrum for the original sample of the compound reported to be $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ dissolved in benzene- d_6 was reported to exhibit three resonances at 2.52, 1.70 and 1.51 ppm with relative integrations of 1:6:6 [7]. The line at 2.52 ppm was assigned to the lone ring proton. The line at 1.70 ppm was assigned to one type of methyl group protons whereas the third line at 1.51 ppm would be for a second type of methyl group protons. Thus, none of the chemical shifts of the resonances in the spectrum of the compound prepared in the current work are in agreement with the original work. The $^1\text{H-NMR}$ spectrum of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ in THF- d_8 in the current work exhibited lines at 3.09, 1.94 and 1.90 ppm for the ring proton and for the two types of methyl group protons, respectively. This spectrum is consistent with the molecular formula of the compound

and demonstrates that the methyl group protons are magnetically very similar. This proposal of magnetically similar methyl groups is supported also by the $^{13}\text{C-NMR}$ spectrum. Two closely spaced resonances at 13.80 and 11.96 ppm were observed for the methyl group carbon atoms whereas the two resonances for the ring carbon atoms occurred at 134.6 and 125.5 ppm. The resonance for the *ipso*-carbon atom bonded to gallium was observed at 65.0 ppm. No $^{13}\text{C-NMR}$ spectral data were reported for the sample originally described as $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ [7].

The compound $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ has very limited solubility in benzene. Thus, a cryoscopic molecular weight study could not be performed as the compound precipitated from a dilute solution as the temperature was lowered to the freezing point of benzene. It should be noted that $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ is less soluble in benzene than either $\text{Ga}(\text{C}_5\text{H}_5)_3$ [9], $\text{Ga}(\text{C}_5\text{Me}_5)_3$ [8], $\text{Ga}(\text{C}_5\text{H}_4\text{Me})_3$ [1] or $\text{Ga}(\text{C}_5\text{H}_4\text{SiMe}_3)_3$ [1]. The ease of crystallization of the compound from solution facilitated the growth of crystals for a potential X-ray structural study. However, the presence of multiple hexagonal-sheets stacked upon one another precluded collection of data and solution of the structure.

The thermal stability of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ was less than $\text{Ga}(\text{C}_5\text{Me}_5)_3$ [8] but significantly higher than either $\text{Ga}(\text{C}_5\text{H}_5)_3$ [9], $\text{Ga}(\text{C}_5\text{H}_4\text{SiMe}_3)_3$ [1] or $\text{Ga}(\text{C}_5\text{H}_4\text{Me})_3$ [1]. Even though no decomposition of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ was observed during simple melting point observations as the melting point was reversible, isomerization occurred over extended time at room temperature according to $^1\text{H-NMR}$ spectroscopy. In contrast, $\text{Ga}(\text{C}_5\text{H}_5)_3$ [9], $\text{Ga}(\text{C}_5\text{H}_4\text{SiMe}_3)_3$ [1] and $\text{Ga}(\text{C}_5\text{H}_4\text{Me})_3$ [1] readily isomerize and then oligomerize at room temperature. Thus, the high thermal stability of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ is consistent with the chemistry of the tetrasubstituted cyclopentadienyl ring. The single ring proton reduces but does not eliminate the potential for a prototropic rearrangement of the $\text{C}_5\text{Me}_4\text{H}$ ring from the preferred structure with the methyl groups in vinyl positions to less thermodynamically favored species with methyl groups in allylic positions. As a structure of vinyl isomers is preferred [10], the tendency for Diels–Alder cycloaddition reactions is reduced due to the steric hindrance of the four methyl groups. It is noteworthy that none of the lines in the $^1\text{H-NMR}$ spectrum that arose from the isomerization of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ upon standing had chemical shifts that matched those originally reported for $\text{Ga}(\text{C}_5\text{H}_4\text{Me})_3$ [7]. The cause for the discrepancy between the observed $^1\text{H-NMR}$ spectrum in the current work and the data reported in the literature is unknown.

A ligand redistribution reaction between GaMe_3 and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ in a 2:1 mol ratio in pentane (Eq. (2)) was investigated as a potential route to $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$.



Even though the ligand redistribution reaction did occur, $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$ was not an isolable compound. After solvent was removed by vacuum distillation from the reaction mixture, the isolated product was identified as $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ with a small quantity of $\text{MeGa}(\text{C}_5\text{Me}_4\text{H})_2$ by the $^1\text{H-NMR}$ spectrum of the sample. Thus, GaMe_3 had been removed with the pentane. Even though neither $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$ nor $\text{Me}_2\text{Ga}(\text{C}_5\text{H}_4\text{SiMe}_3)$ form isolable single compounds, $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$ exhibits different chemistry than does $\text{Me}_2\text{Ga}(\text{C}_5\text{H}_4\text{SiMe}_3)$ [1]. The tetramethyl derivative $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$ reverts readily to the starting materials whereas $\text{Me}_2\text{Ga}(\text{C}_5\text{H}_4\text{SiMe}_3)$ [1] forms a mixture of $\text{Me}_n\text{Ga}(\text{C}_5\text{H}_4\text{SiMe}_3)_{3-n}$ ($n = 1, 2, 3$). Experimental evidence for the occurrence of the ligand redistribution reaction between GaMe_3 and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ to form $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$ was obtained by combining the reagents in a 2:1 mol ratio in benzene- d_6 and examining the $^1\text{H-NMR}$ spectrum of the resulting solution. The resonances in the spectrum were consistent with the products of a ligand redistribution reaction (Eq. (3)). The principal gallium–methyl resonance is due to $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$



whereas the two less intense resonances are assigned to GaMe_3 and $\text{MeGa}(\text{C}_5\text{Me}_4\text{H})_2$. The extent of the ligand redistribution equilibrium (Eq. (3)) in solution was determined by calculating the equilibrium constant by using the integration values from the $^1\text{H-NMR}$ spectrum. The constant for a benzene solution at the normal operating temperature of the instrument was 3.2×10^{-3} whereas the constant for a THF solution was 1.4×10^{-2} . These values are similar to those previously reported for THF solutions of $\text{Me}_2\text{Ga}(\text{C}_5\text{H}_5)$ ($K = 1.4 \times 10^{-1}$) [2], $\text{Et}_2\text{Ga}(\text{C}_5\text{H}_5)$ ($K = 1.3 \times 10^{-2}$) [3], $\text{Me}_2\text{Ga}(\text{C}_5\text{H}_4\text{Me})$ ($K = 2.3 \times 10^{-2}$) [1], $\text{Et}_2\text{Ga}(\text{C}_5\text{H}_4\text{Me})$ ($K = 1.5 \times 10^{-2}$) [1], $\text{Me}_2\text{Ga}(\text{C}_5\text{H}_4\text{SiMe}_3)$ ($K = 2.8 \times 10^{-3}$) [1]. Apparently, the stability of R_2GaCp ($\text{R} = \text{Me}, \text{Et}; \text{Cp} = \text{C}_5\text{H}_5, \text{C}_5\text{H}_4\text{Me}, \text{C}_5\text{H}_4\text{SiMe}_3, \text{C}_5\text{HMe}_4$) as a pure compound has little or no bearing on the nature of the solution equilibrium, as all of the ligand redistribution reactions, whether they lead to isolable compounds or not, form redistribution equilibria in solution with similar constants.

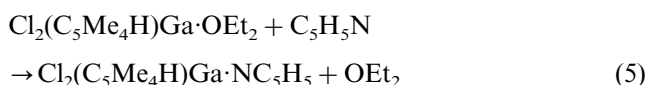
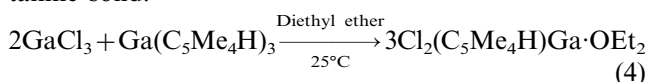
The synthesis of the chloride derivatives $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ [7] and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$ by both metathetical and stoichiometric ligand redistribution reactions were investigated but neither compound could be isolated. In contrast, both of the corresponding pentamethylcyclopentadienyl derivatives $\text{Ga}(\text{C}_5\text{Me}_5)_2\text{Cl}$ and $\text{Ga}(\text{C}_5\text{Me}_5)\text{Cl}_2$ have been isolated as pure compounds [11]. When attempts were made to prepare

$\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ by reacting GaCl_3 and $\text{Li}(\text{C}_5\text{Me}_4\text{H})$ in a 1:2 mol ratio in diethyl ether at 0°C , the initial isolated product was a mixture of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$, and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$. The first crop of crystals after recrystallization of this product from ether was a mixture of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$, whereas later crops were mixtures of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$. Elemental analyses (carbon, hydrogen and chlorine) of the initial crop of crystals supported the presence of a mixture of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ as the experimental percent carbon and hydrogen were significantly higher than the theoretical values for $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ whereas the experimental percent chlorine was lower. Later crops of crystals were slightly yellowish and had elemental analysis for carbon and hydrogen that were lower than the theoretical values for $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$. Furthermore, earlier crops of crystals melted at higher temperatures ($199\text{--}215^\circ\text{C}$) than did later crops ($180\text{--}185^\circ\text{C}$). If the elemental analyses for carbon and hydrogen for the initial and later crops of crystals are averaged, the average values are closer to the theoretical values for $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ than are the elemental analyses reported for $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ [7]. The original elemental analyses for carbon and hydrogen for the product reported as being $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ were higher than the calculated values by 1.03 and 0.25%, respectively, whereas chlorine was low by 0.30% [7]. The literature states that two crops of crystals were collected. If they had been combined prior to elemental analysis, high results for carbon and hydrogen might be possible. No melting point for a sample suggested as being $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ was reported in the original paper [7].

When the product from the attempted preparation of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ from GaCl_3 and $\text{Li}(\text{C}_5\text{Me}_4\text{H})$ was isolated after removal of ether by vacuum distillation but not recrystallized, a colorless solid was obtained. Partial separation of this colorless solid by a single pentane extraction yielded a pentane soluble fraction that was predominantly $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ with some $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$. The pentane insoluble fraction was a mixture of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$, and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$. The $^1\text{H-NMR}$ spectrum of this mixture suggested slight isomerization of the cyclopentadienyl rings. When the colorless solid was allowed to stand at room temperature overnight, the entire sample isomerized to a purple solid which decomposed to a brown solid at $80\text{--}85^\circ\text{C}$. All data suggest that $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ undergoes a ligand redistribution reaction to form an equilibrium mixture with $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$. Thus, the experimental results suggest that it is highly doubtful that the previous workers isolated pure $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$.

Attempts to synthesize $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$ by both metathetical and ligand redistribution reactions in ei-

ther diethyl ether or pentane were unsuccessful. Previous workers [7] did not report a synthesis of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$. A metathetical reaction between GaCl_3 and $\text{Li}(\text{C}_5\text{Me}_4\text{H})$ in a 1:1 mol ratio in diethyl ether at 0 °C produced a cloudy brown viscous material from which the Et_2O could not be removed. A ligand redistribution reaction between $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ and GaCl_3 in a 1:2 mol ratio in pentane yielded an insoluble orange–brown material. Since $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$ appeared to possibly form an adduct with Et_2O , a stoichiometric quantity of pyridine was added to an Et_2O solution of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ and GaCl_3 in a 1:2 mol ratio (Eqs. (4) and (5)). The isolated product was the adduct $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}\cdot\text{pyridine}$, a bright yellow–green crystalline solid.



The analytically pure adduct had a melting point of 151–155 °C and was monomeric in benzene solution according to a cryoscopic molecular weight study. The $^1\text{H-NMR}$ spectrum was typical of that expected for the 1:1 adduct dissolved in benzene- d_6 .

The structure of $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}\cdot\text{pyridine}$ was determined by a single crystal X-ray diffraction study. The compound crystallizes in space group $Pbca$ with $Z = 16$; there are therefore two independent molecules in the crystallographic ‘asymmetric unit’. The molecular geometry and labeling of the atoms for one such molecule (A) is depicted in Fig. 1, while important bond distances and angles for both molecules A and B are collected in Table 1. The molecular geometry reveals a monomeric gallium–nitrogen adduct with the molecules separated by normal van der Waals distances. The two

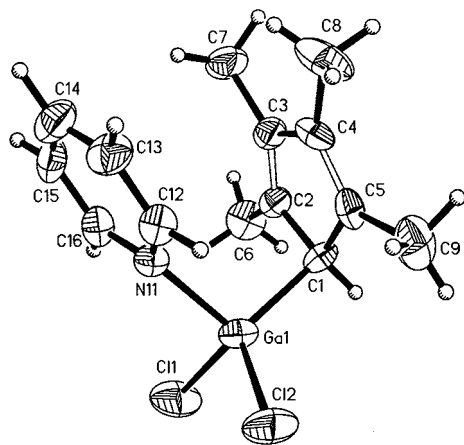


Fig. 1. Labeling of atoms in the $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}\cdot\text{pyridine}$ molecule (molecule A). The 30% probability envelopes are shown for the vibration ellipsoids of all non-hydrogen atoms, while hydrogen atoms are artificially reduced.

Table 1
Selected bond lengths (Å) and bond angles (°) for $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}\cdot\text{pyridine}$

Molecule A		Molecule B	
<i>Gallium–ligand distances</i>			
Ga(1)–Cl(1)	2.186(2)	Ga(2)–Cl(3)	2.180 (2)
Ga(1)–Cl(2)	2.181(2)	Ga(2)–Cl(4)	2.189(2)
Ga(1)–C(1)	1.989(6)	Ga(2)–C(21)	1.980(7)
Ga(1)–N(11)	1.993(5)	Ga(2)–N(31)	1.994(5)
<i>Distances within C₅Me₄H ligands</i>			
C(1)–C(2)	1.470(8)	C(21)–C(22)	1.470(8)
C(2)–C(3)	1.345(9)	C(22)–C(23)	1.349(9)
C(3)–C(4)	1.442(9)	C(23)–C(24)	1.438(9)
C(4)–C(5)	1.347(9)	C(24)–C(25)	1.334(9)
C(5)–C(1)	1.487(9)	C(25)–C(21)	1.469(9)
C(2)–C(6)	1.509(9)	C(22)–C(26)	1.500(9)
C(3)–C(7)	1.517(8)	C(23)–C(27)	1.507(8)
C(4)–C(8)	1.491(9)	C(24)–C(28)	1.493(9)
C(5)–C(9)	1.510(9)	C(25)–C(29)	1.518(8)
<i>Distances within pyridine ligand</i>			
N(11)–C(12)	1.332(8)	N(31)–C(32)	1.325(8)
C(12)–C(13)	1.345(10)	C(32)–C(33)	1.367(10)
C(13)–C(14)	1.357(11)	C(33)–C(34)	1.357(11)
C(14)–C(15)	1.355(12)	C(34)–C(35)	1.345(10)
C(15)–C(16)	1.352(10)	C(35)–C(36)	1.372(9)
C(16)–N(11)	1.351(8)	C(36)–N(11)	1.335(8)
<i>Angles around gallium atom</i>			
Cl(1)–Ga(1)–Cl(2)	106.8(1)	Cl(3)–Ga(2)–Cl(4)	106.0(1)
Cl(1)–Ga(1)–C(1)	117.2(2)	Cl(3)–Ga(2)–C(21)	118.0(2)
Cl(1)–Ga(1)–N(11)	103.8(2)	Cl(3)–Ga(2)–N(31)	104.4(1)
Cl(2)–Ga(1)–C(1)	119.1(2)	Cl(4)–Ga(2)–C(21)	118.1(2)
Cl(2)–Ga(1)–N(11)	104.1(1)	Cl(4)–Ga(2)–N(31)	103.4(1)
C(1)–Ga(1)–N(11)	103.9(2)	C(21)–Ga(2)–N(31)	105.1(2)
<i>Angles within C₅ ring</i>			
C(5)–C(1)–C(2)	104.6(5)	C(25)–C(21)–C(22)	104.6(5)
C(1)–C(2)–C(3)	108.1(5)	C(21)–C(22)–C(23)	107.6(5)
C(2)–C(3)–C(4)	109.9(5)	C(22)–C(23)–C(24)	109.7(5)
C(3)–C(4)–C(5)	109.1(5)	C(23)–C(24)–C(25)	108.8(6)
C(4)–C(5)–C(1)	108.0(5)	C(24)–C(25)–C(21)	108.8(5)

independent molecules are chemically equivalent with a central gallium(III) atom linked to two chloride ligands ($\text{Ga}–\text{Cl} = 2.180(2)–2.189(2)$ Å), an $\eta^1\text{-C}_5\text{Me}_4\text{H}$ ligand ($\text{Ga}–\text{C} = 1.980(7)–1.989(6)$ Å) and a pyridine ligand ($\text{Ga}–\text{N} = 1.993(5)$ Å). The gallium–chlorine distances are comparable to the terminal $\text{Ga}–\text{Cl}$ distance in $[\text{Ga}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ of 2.124(4) Å [11] but slightly shorter than the corresponding distance in the adduct $\text{Cl}(\text{PhMe}_2\text{CCH}_2)_2\text{Ga}\cdot\text{NH}_2(t\text{-Bu})$ of 2.261(2) Å [12], and longer than the terminal distances in $[\text{GaCl}_3]_2$ of 2.06(3) Å [13]. The gallium–carbon distance is comparable to the $\text{Ga}–\text{C}$ distance in $[\text{Ga}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2$ of 1.97(1) Å [8] and the average $\text{Ga}–\text{C}$ distance in $\text{Ga}(\text{C}_5\text{H}_5)_3$ of 2.05(3) Å [9] and in $\text{Ga}(\text{C}_5\text{Me}_5)_3$ of 2.037(4) Å [7]. The gallium–nitrogen distance is shorter than the corresponding distance in the adduct $\text{Cl}(\text{PhMe}_2\text{CCH}_2)_2\text{Ga}\cdot\text{NH}_2(t\text{-Bu})$ of 2.093(7) Å [12].

The central gallium(III) atoms in $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}$ -pyridine have distorted tetrahedral coordination environment; the largest interligand angles are the $\text{Cl-Ga-C}_5\text{Me}_4\text{H}$ angles ($117.2(2)$ – $119.1(2)^\circ$) while the Cl-Ga-N angles ($103.4(1)$ – $104.4(1)^\circ$) and C-Ga-N angles ($103.9(2)$ – $105.1(2)^\circ$) are the smallest. Bond lengths within the $\text{C}_5\text{Me}_4\text{H}$ systems are such that the C=C = $1.334(9)$ – $1.349(9)$ Å, the central $\text{C}(\text{sp}^2)$ – $\text{C}(\text{sp}^2)$ system has C-C = $1.438(9)$ – $1.442(9)$ Å, the $\text{C}(\text{sp}^3)$ – $\text{C}(\text{sp}^2)$ distances are $1.469(9)$ – $1.487(9)$ Å, and the eight $\text{C}(\text{sp}^2)$ – Me distances range from $1.491(9)$ to $1.518(8)$ Å.

Our attempt to prepare a pyridine adduct of the monochloride derivative $\text{Cl}(\text{C}_5\text{Me}_4\text{H})_2\text{Ga}$ -pyridine by adding pyridine to an Et_2O solution that had $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ and GaCl_3 in a 2:1 mol ratio was unsuccessful. Separation of the isolated product into two fractions by recrystallization of an ether solution at -30°C provided a crystalline solid and a soluble residue. The $^1\text{H-NMR}$ spectra of these fractions were consistent with mixtures of $(\text{C}_5\text{Me}_4\text{H})_3\text{Ga}$ -pyridine, $\text{Cl}(\text{C}_5\text{Me}_4\text{H})_2\text{Ga}$ -pyridine and $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}$ -pyridine in different ratios. Thus, either $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}$ or the adduct must undergo a ligand redistribution reaction to form an equilibrium mixture of these various compounds.

3. Experimental

All compounds described in this investigation were exceedingly sensitive to oxygen and moisture and were manipulated either under a purified argon atmosphere in a Vacuum Atmospheres drybox or by using standard vacuum line techniques. All solvents were dried by conventional procedures. Tetramethylcyclopentadiene $\text{C}_5\text{Me}_4\text{H}_2$ was purchased from Aldrich Chemical Co. and vacuum distilled prior to use. The reagent $\text{Li}(\text{C}_5\text{Me}_4\text{H})$ was prepared by adding a solution of $\text{Li}(n\text{-Bu})$ in hexane/pentane to an excess of $\text{C}_5\text{Me}_4\text{H}$ at 0°C . The insoluble product was washed three times with the reaction solvent and then thoroughly dried under vacuum. Elemental analyses were performed by E&R Microanalytical Laboratory, Parsippany, NJ. Melting points were determined with a Mel-Temp by using flame sealed capillaries filled with argon and are uncorrected. Infrared spectra of samples as either Nujol mulls between CsI plates were recorded by using a Perkin–Elmer 683 spectrometer. $^1\text{H-NMR}$ (400 MHz) and $^{13}\text{C-NMR}$ (125.7 MHz) spectra were recorded with Varian VXR-400 and Varian VXR-500 spectrometers, respectively. Proton chemical shifts are reported in δ (ppm) units and are referenced to SiMe_4 at δ 0.00 ppm and either $\text{C}_6\text{D}_5\text{H}$ at δ 7.15 or the residual proton in the other deuterated solvents, as appropriate. Carbon-13 chemical shifts are referenced to SiMe_4 at δ 0.00 ppm and to C_6D_6 at δ 128.39 ppm. All samples for

NMR spectra were contained in flame sealed NMR tubes. Molecular weights were measured cryoscopically for benzene solutions by using an instrument similar to that described by Shriver and Drezdson [14].

3.1. Synthesis of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$

A Solv-Seal tube containing 0.66 g (3.8 mmol) of GaCl_3 dissolved in approximately 40 ml of Et_2O was attached via a frit to a Solv-Seal Schlenk flask containing 1.38 g (11.3 mmol) of $\text{Li}(\text{C}_5\text{Me}_4\text{H})$. The solution of GaCl_3 was added to the $\text{Li}(\text{C}_5\text{Me}_4\text{H})$ at 0°C and stirred overnight. The resulting pale yellow mixture was filtered and placed in a bath and the temperature was gradually lowered to -40°C over a period of 3 days. Colorless crystals were isolated by cold-filtration and then removal of the Et_2O by vacuum distillation. Nine crops of crystals were collected with concentration of the solution as necessary to give a total of 1.21 g (mmol) of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ (74.6% yield based on GaCl_3). The crystallized compound was free of lithium and chloride ions according to a flame test and the addition of 5% $\text{AgNO}_3(\text{aq})$ to a sample that had been hydrolyzed in dilute aqueous nitric acid. The compound was not sufficiently soluble in benzene for a cryoscopic molecular weight study. $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$: Colorless crystalline solid, slightly soluble in Et_2O , pentane, and benzene. M.p. 225 – 227.5°C . $^1\text{H-NMR}$ (C_6D_6 , δ): 3.22 (s, 0.9, ring-H), 1.95 (s, 12, CH_3); ($\text{THF-}d_8$, δ): 3.09 (s, 0.87, ring-H), 1.94 (s, 6.0, CH_3), 1.90 (s, 6.0, CH_3); $^{13}\text{C-NMR}$ (C_6D_6 , δ): 134.63 (vinyl ring-C), 125.51 (vinyl ring-C), 65.0 (allyl ring-C), 13.80 (CH_3), 11.96 (CH_3). IR (Nujol mull, cm^{-1}): 1575 (w), 1230 (s), 1130 (w), 1100 (w), 1065 (w), 1030 (w), 1005 (vw), 955 (w), 915 (w), 835 (vs), 690 (m), 635 (m), 555 (m), 460 (s). Anal. Calc. for $\text{C}_{27}\text{H}_{39}\text{Ga}$: C, 74.84; H, 9.07. Found: C, 74.85; H, 9.17%.

3.2. Attempted synthesis of $\text{Me}_2\text{Ga}(\text{C}_5\text{Me}_4\text{H})$

A preweighed sample of GaMe_3 (1.66 g, 1.45 mmol) was vacuum distilled onto 0.266 g (0.614 mmol) of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ dissolved in pentane and the resulting solution was stirred for 3 days. The material volatile at -78°C was removed to leave a colorless solid (0.247 g, 92.6% recovery if pure $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$). The pentane that had been removed was observed to ‘smoke’ in the presence of air, an indication of the presence of GaMe_3 . The ^1H and $^{13}\text{C-NMR}$ spectra indicated that the colorless solid was $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ with a small amount of $\text{MeGa}(\text{C}_5\text{Me}_4\text{H})_2$ ($\sim 12\%$ based on integration of the NMR spectrum). Colorless Solid (impure $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$): $^1\text{H-NMR}$ (C_6D_6 , δ): 3.22 (s, 0.7, ring-H), 1.95 (s, 12.0, ring- CH_3), -1.09 (s, 0.13, GaCH_3); $^{13}\text{C-NMR}$ (C_6D_6 , δ): 134.59 (vinylic ring-C), 125.48 (vinylic ring-

C), 64.98 (allylic ring-C), 13.77 (ring-CH₃), 11.93 (ring-CH₃).

3.3. ¹H-NMR spectral study of solution formed by combining GaMe₃ and Ga(C₅Me₄H)₃ in a 2:1 mol ratio

A small vessel connected to an NMR tube was charged with 0.0811 g (0.187 mmol) of Ga(C₅Me₄H)₃. The solvent C₆D₆ and then 0.0427 g (0.372 mmol) of GaMe₃ were added via vacuum distillation. The resulting solution was stirred and then poured into the NMR tube. An analogous experiment was performed by using THF-*d*₈, 0.0320 g (0.0738 mmol) of Ga(C₅Me₄H)₃ and 0.0179 g (0.155 mmol) of GaMe₃. The ¹H-NMR spectra of both solutions indicated the presence of an equilibrium mixture of multiple species. ¹H-NMR (C₆D₆, δ): 4.79 (s, 0.4, vinylic ring-H), 3.22 (s, 0.2, allylic ring-H), 1.95/1.93/1.90 (s/s-br/s, 12.0, ring-Me's), -0.35 (s-br, 4.9, GaMe₂ and GaMe₃), -1.09 (s-br, 0.1, GaMe); ¹H-NMR (THF-*d*₈, δ): 3.90 (s, 0.7, Me₂Ga(C₅Me₄H)·THF), 3.25 (s, 0.2, MeGa(C₅Me₄H)₂·THF), 1.95/1.80 (s/s, 2.7/3.0, MeGa(C₅Me₄H)₂·THF), 1.92/1.79 (s/s, 6.0/5.7, Me₂Ga(C₅Me₄H)·THF), -0.49 (s, 1.2, GaMe₃·THF), -0.61 (s, 6.1, Me₂Ga(C₅Me₄H)·THF), -0.82 (s, 0.3, MeGa(C₅Me₄H)₂·THF).

3.4. Attempted synthesis of Ga(C₅Me₄H)₂Cl by a metathetical reaction

(a) The synthesis of Ga(C₅Me₄H)₂Cl was attempted in Sov-Seal glassware by adding 0.271 g (1.54 mmol) of GaCl₃ dissolved in 50 ml of diethyl ether to 0.394 g (3.08 mmol) of Li(C₅Me₄H) contained in a flask maintained at 0°C. The reaction mixture was stirred and permitted to warm to room temperature overnight. The resulting pale yellow solution was filtered and then recrystallized at -25°C. A colorless crystalline solid (0.0656 g) was isolated by filtering the cold mixture. Collection of additional crops of crystals was not attempted. M.p. 210–215°C (dec. to dark grayish solid), 220°C (melts to a purple liquid). ¹H-NMR (C₆D₆, δ): 3.48 (s, <0.1, ring-H, Ga(C₅Me₄H)₂Cl), 3.22 (s, 1.7, ring-H, Ga(C₅Me₄H)₃), 2.02 (s, 1.4, ring-CH₃, Ga(C₅Me₄H)₂Cl), 1.95 (s, 24, ring-CH₃, Ga(C₅Me₄H)₃), 1.81 (s, 1.4, ring-CH₃, Ga(C₅Me₄H)₂Cl). Anal. Calc. for C₁₈H₂₆ClGa: C, 62.20; H, 7.54; Cl, 10.20. Found: C, 68.95; H, 8.19; Cl, 2.83%.

(b) The synthesis of Ga(C₅Me₄H)₂Cl was attempted a second time by using the same procedure as described above. Thus, 0.650 g (3.69 mmol) of GaCl₃ dissolved in 50 ml of diethyl ether was added to 0.945 g (7.38 mmol) of Li(C₅Me₄H) at 0°C. The resulting pale yellow solution was filtered through a frit and then recrystallized at -40°C over a period of 3 days. After the mixture was cold filtered through a frit, 0.106 g of colorless crystals was isolated. Three additional crops of crystals with

concentration of the solution, as necessary, gave a total of 0.753 g of a crystalline solid. The colorless product was observed to decompose/isomerize to a purple solid at room temperature under either an argon atmosphere or vacuum. The second crop of crystals tested positive for chloride ion. Crop 1 — mostly Ga(C₅Me₄H)₃: colorless crystalline solid, soluble in Et₂O, benzene. M.p. 199–203.5°C (dec. to dark grayish solid), 212–215°C (melts to a purple liquid). ¹H-NMR (C₆D₆, δ): 3.22 (s, 1.7, allylic ring-H), 1.95 (s, 24.0, ring-Me); ¹³C-NMR (C₆D₆, δ): 134.60 (vinyl ring-C), 125.48 (vinyl ring-C), 64.98 (allyl ring-C), 13.77 (ring-CH₃), 11.93 (ring-CH₃). Crop 4: Anal. Calc. for C₁₈H₂₆ClGa: C, 62.20; H, 7.54. Found: C, 53.82; H, 7.04%.

3.5. Attempted synthesis of Ga(C₅Me₄H)₂Cl by a ligand redistribution reaction

A Solv-Seal tube containing 0.099 g (0.56 mmol) of GaCl₃ dissolved in ca. 40 ml of Et₂O was attached via a frit to a Solv-Seal Schlenk flask containing 0.491 g (1.13 mmol) of Ga(C₅Me₄H)₃. The solution of GaCl₃ was added to the Ga(C₅Me₄H)₃ at room temperature and stirred overnight. The colorless solution was concentrated to saturation, filtered and recrystallized by cooling at -35°C for 11 days. A colorless solid crystallized on the bottom of the tube while a slightly yellowish solid formed on the wall of the finger tube at a height corresponding to the depth of solvent in the -35°C bath. The Et₂O solution was cold filtered and 0.0913 g of colorless crystals and 0.187 g of a light yellow solid were isolated. Colorless solid — impure Ga(C₅Me₄H)₃: soluble in Et₂O, benzene. M.p. 212–222°C (dec. to a gray-brown solid then melts to a purple liquid). ¹H-NMR (C₆D₆, δ): 3.22 (s, 1.1, ring-H), 1.95 (s, 24.0, ring-Me). Light yellow solid — mixture of Ga(C₅Me₄H)₂Cl and Ga(C₅Me₄H)₃: soluble in Et₂O, benzene. M.p. (light yellow part): 180–185°C (dec. to a purple liquid); mp (colorless portion): 199–206°C (dec. to a purple liquid).

3.6. Attempted synthesis of Ga(C₅Me₄H)Cl₂ by a metathetical reaction

The synthesis of Ga(C₅Me₄H)Cl₂ from 1.19 g (6.77 mmol) of GaCl₃ and 0.867 g (6.77 mmol) of Li(C₅Me₄H) in Et₂O was attempted by using a procedure analogous to that described previously for the attempted synthesis of Ga(C₅Me₄H)₂Cl. No solid formed after the attempted recrystallization at -40°C even after several successive concentrations of the solution. Removal of the solvent yielded a cloudy, non-volatile brown liquid. ¹H-NMR (C₆D₆, δ): 3.32 (q, 7.2, OCH₂CH₃), 2.13 (s, 6.0, ring-Me), 1.80 (s, 6.5, ring-Me), 0.91 (t, 9.5, OCH₂CH₃).

3.7. Attempted synthesis of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$ by a ligand redistribution reaction in pentane

A sample of GaCl_3 (0.312 g, 1.77 mmol) dissolved in about 40 ml of pentane was added via a frit to a Solv-Seal Schlenk flask containing $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ (0.383 g, 0.884 mmol). A yellow–orange precipitate formed immediately. The mixture was stirred overnight and solvent was removed by vacuum distillation to yield 0.606 g of an orange–brown solid (87.2% by mass of theoretically expected $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$ based on $\text{Ga}(\text{C}_5\text{HMe}_4)_3$). Orange–brown solid: soluble in THF, insoluble in pentane. M.p. 60–67°C (dec. to a purple–brown goo). $^1\text{H-NMR}$ (THF- d_8 , δ): multiple lines indicative of isomerization and possible oligomerization.

3.8. Attempted synthesis of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2$ by a ligand redistribution reaction in Et_2O

A sample of GaCl_3 (0.283 g, 1.61 mmol) dissolved in about 25 ml of Et_2O was added via a frit to a Solv-Seal Schlenk flask containing $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ (0.349 g, 0.805 mmol) and stirred overnight. The resulting clear solution was filtered and then the Et_2O was removed to leave a yellowish goo. About 10–15 ml of Et_2O was distilled onto the goo and a clear solution reformed. The solution was placed in a bath at -25°C and colorless needle-shaped crystals formed after 3 days. The solution was cold-filtered. Removal of the solvent provided a brown goo similar to that obtained from the metathetical reaction. During the time required to take the apparatus into the dry box, the crystals (0.361 g) had become opaque and slightly purplish. The crystals tested positive for chloride ion. The crystalline solid became purple upon standing at room temperature. M.p. 80–85°C (dec. to purple–brown liquid). $^1\text{H-NMR}$ (C_6D_6 , δ): 3.29 (q 6.8 Hz, 4.8, OCH_2CH_3), 3.14 (s–br, 0.6, ring-H), 2.12 (s, 6.0, ring- CH_3), 1.74 (s, 6.4, ring- CH_3), 0.67 (t 6.8 Hz, 6.9, OCH_2CH_3), $^{13}\text{C-NMR}$ (C_6D_6 , δ): 134.89 (s, ring-C), 131.11 (s, ring-C), 68.21 (s, ring-C), 44.83 (s, OCH_2CH_3), 13.92 (s, ring- CH_3), 13.48 (s, OCH_2CH_3), 11.37 (s, ring- CH_3).

3.9. Synthesis of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2\cdot\text{NC}_5\text{H}_5$ by a ligand redistribution reaction

A Schlenk flask containing 0.326 g (0.752 mmol) of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ was connected via an elbow joint to a round-bottom flask containing 0.265 g (1.50 mmol) of GaCl_3 . Approximately 50 ml of Et_2O and then 0.179 g (2.26 mmol) of pyridine was vacuum distilled into the round-bottom flask. The reagents were combined in the Schlenk flask and a clear, bright yellow solution formed. The apparatus was placed -15°C bath and bright yellow–green crystals formed overnight. The solution was decanted from the crystals and then sol-

vent was removed by vacuum distillation. To give 0.224 g of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2\cdot\text{NC}_5\text{H}_5$. A second crop that formed at -30°C weighed 0.435 g for a total of 0.659 g (1.93 mmol, 85.7% yield based on GaCl_3) of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2\cdot\text{NC}_5\text{H}_5$. A crystal from the first crop was used for the X-ray structural study. $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2\cdot\text{NC}_5\text{H}_5$: brittle, bright yellow–green crystalline solid. M.p. 151–155°C. $^1\text{H-NMR}$ (C_6D_6 , δ): 7.94 (m, 1.6, NC_5H_5 , $m\text{-H}$), 6.56 (m, 0.8, NC_5H_5 , $p\text{-H}$), 6.16 (m, 1.6, NC_5H_5 , $o\text{-H}$), 3.47 (s, 0.7, ring-H), 2.14 (s, 6.0, ring- CH_3), 1.30 (s, 6.1, ring- CH_3); $^{13}\text{C-NMR}$ (C_6D_6 , δ): 146.51 (s, NC_5H_5), 140.96 (s, NC_5H_5), 133.61 (s, ring-C), 131.51 (s, ring-C), 124.19 (s, NC_5H_5), 14.30 (s, ring- CH_3), 11.16 (s, ring- CH_3). Anal. Calc. for $\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{GaN}$: C, 49.33; H, 5.32. Found: C, 49.23; H, 5.31%. Cryoscopic molecular weight, benzene solution, F_w 340.93 (molality, obs. mol. wt., assoc.): 0.0608, 343, 1.01; 0.0413, 323, 0.95.

3.10. Attempted synthesis of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}\cdot\text{NC}_5\text{H}_5$

A Schlenk flask containing 0.784 g (1.81 mmol) of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ was connected via a frit to a round-bottom flask containing 0.159 g (0.905 mmol) of GaCl_3 dissolved in ca. 50 ml of Et_2O . The pyridine (0.364 g, 4.60 mmol) was added by vacuum distillation to the solution of GaCl_3 . The reagents were combined in the Schlenk flask and stirred overnight to give a clear, bright yellow solution. After the apparatus was placed in a -40°C bath overnight, 0.369 g of a yellow–orange crystalline solid mixed with a yellowish powder were isolated. The solution that was separated from the solid by filtration produced 0.637 g of a yellow–green solid after the solvent was removed by vacuum distillation. The $^1\text{H-NMR}$ spectra of the two solids were consistent with mixtures of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3\cdot\text{NC}_5\text{H}_5$, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}\cdot\text{NC}_5\text{H}_5$ and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2\cdot\text{NC}_5\text{H}_5$. Yellow–orange solid: $^1\text{H-NMR}$ (C_6D_6 , δ): 8.17 (br–overlapping, NC_5H_5 , $m\text{-H}$), 7.70 (br–overlapping, NC_5H_5 , $m\text{-H}$), 6.73 (br, NC_5H_5 , $p\text{-H}$), 6.35 (br, NC_5H_5 , $o\text{-H}$), 3.72 (s, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}\cdot\text{NC}_5\text{H}_5$), 3.47 (br, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2\cdot\text{NC}_5\text{H}_5$ and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3\cdot\text{NC}_5\text{H}_5$), 2.14 (s–overlapping, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2\cdot\text{NC}_5\text{H}_5$), 2.07 (s–overlapping, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}\cdot\text{NC}_5\text{H}_5$), 2.02 (br–overlapping, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3\cdot\text{NC}_5\text{H}_5$), 1.77 (br–overlapping, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3\cdot\text{NC}_5\text{H}_5$), 1.70 (s–overlapping, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}\cdot\text{NC}_5\text{H}_5$), 1.30 (s, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2\cdot\text{NC}_5\text{H}_5$). Yellow–green solid: $^1\text{H-NMR}$ (C_6D_6 , δ): 8.05 (br, NC_5H_5 , $m\text{-H}$), 7.67 (br, NC_5H_5 , $m\text{-H}$), 6.66 (m, NC_5H_5 , $p\text{-H}$), 6.28 (m, NC_5H_5 , $o\text{-H}$), 3.73 (s, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}\cdot\text{NC}_5\text{H}_5$), 3.47/3.42 (s/br–overlapping, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2\cdot\text{NC}_5\text{H}_5$ and $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3\cdot\text{NC}_5\text{H}_5$), 2.14 (s–overlapping, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2\cdot\text{NC}_5\text{H}_5$), 2.08 (br–overlapping, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl}\cdot\text{NC}_5\text{H}_5$), 2.01 (br–overlapping, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3\cdot\text{NC}_5\text{H}_5$), 1.80 (br–overlapping,

$\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3 \cdot \text{NC}_5\text{H}_5$, 1.69 (s, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_2\text{Cl} \cdot \text{NC}_5\text{H}_5$), 1.29 (s, $\text{Ga}(\text{C}_5\text{Me}_4\text{H})\text{Cl}_2 \cdot \text{NC}_5\text{H}_5$).

3.11. $^1\text{H-NMR}$ spectral study of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$ with excess pyridine

Approximately 5 mg of $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3$, an excess of pyridine and C_6D_6 were combined in an NMR tube. The $^1\text{H-NMR}$ spectrum exhibited broad lines indicative of exchange between $\text{Ga}(\text{C}_5\text{Me}_4\text{H})_3 \cdot \text{NC}_5\text{H}_5$ and free pyridine. $^1\text{H-NMR}$ (C_6D_6 , δ): 8.52 (br, 5.9, NC_5H_5 , *m-H*), 6.96 (br, 2.7, NC_5H_5 , *p-H*), 6.65 (br, 5.4, NC_5H_5 , *o-H*), 3.48 (s-br, 3.3, ring- H), 2.04 (br, 18.0, ring- CH_3), 1.75 (s-br, 20.9, ring- CH_3).

3.12. X-ray diffraction studies. Collection of X-ray diffraction data and structural solution for $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}$ pyridine

A pale yellow crystal ($0.36 \times 0.47 \times 0.62 \text{ mm}^3$) was sealed into a glass capillary and mounted on a Siemens R3m/V diffractometer. The crystal's Laue symmetry (*mmm*), crystal class (orthorhombic), orientation matrix and cell dimensions were determined as described previously [15]. Details are provided in Table 2.

Table 2
Data for X-ray crystallographic studies of $\text{Cl}_2(\text{C}_5\text{Me}_4\text{H})\text{Ga}$ pyridine

Molecular formula	$\text{C}_{14}\text{H}_{18}\text{Cl}_2\text{GaN}$
M_r	340.9
Crystal system	orthorhombic
Space group	<i>Pbca</i> (no. 61)
a (Å)	17.050(5)
b (Å)	14.301(5)
c (Å)	26.016(10)
V (Å ³)	6344(4)
D_{calc} (g cm^{-3})	1.428
Z	16
μ (Mo-K α) (mm^{-1})	2.052
T (K)	296
Scan mode	$2\theta-\theta$
2θ range (°)	6.0–45.0
h	0 to 18
k	0 to 15
l	–28 to +28
Reflections collected	8915
Unique reflections	4154 ($R_{\text{int}} = 1.54\%$)
Reflections used for refinement ($I > 2\sigma(I)$)	2454
Absorption correction	ψ -scans
$T_{\text{min}}/T_{\text{max}}$	0.2826/0.3219
Refined parameters	336
Final R indices (all data) ^a	$R = 7.30$, $wR = 4.36\%$
Final R indices (obs. data) ^a	$R = 3.87$, $wR = 3.49\%$, ($ F_o > 4\sigma(F_o)$)
Largest difference peak and hole ($\text{e} \text{ \AA}^{-3}$)	0.29 and -0.30

^a R indices are defined as follows: $R(\%) = 100 \sum ||F_o| - |F_c|| / \sum |F_o|$;
 $wR(\%) = 100 [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

Data were corrected for Lp factors and for absorption. The systematic absences ($0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, $hk0$ for $h = 2n + 1$) uniquely define the common centrosymmetric space group *Pbca* [16].

Crystallographic computations were carried out with the use of the SHELXTL PLUS (Release 4.11(VMS)) program package [17]. The analytical neutral atom scattering factors were corrected for both real and imaginary components of anomalous dispersion [18]. The structure was solved by a combination of Patterson synthesis, difference Fourier syntheses and least-squares refinement. All non-hydrogen atoms were located and refined anisotropically. Hydrogen atoms were located and included in idealized positions based upon $d(\text{C-H}) = 0.96 \text{ \AA}$ [19]. Their thermal parameters were refined (with those of the methyl groups in each ligand and refined as a single parameter). The final discrepancy index was $R = 3.87\%$ for those reflections with $|F_o| > 4\sigma(|F_o|)$.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 154043. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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