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Homoleptic and Heteroleptic Gallium(III) Compounds Containing Monosubstituted Cyclopentadienyl Ligands: $Ga(C_5H_4Me)_3$, $Ga(C_5H_4SiMe_3)_3$, and $R_2Ga(C_5H_4Me)$ (R = Me, Et)

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The new gallium(III) cyclopentadienyl derivatives $Ga(C_5H_4Me)_3$ and $Ga(C_5H_4SiMe_3)_3$ have been synthesized by metathetical reactions. Subsequent stoichiometric ligand redistribution reactions with GaR_3 (R = Me, Et) were used to prepare $R_2Ga(C_5H_4Me)$ as pure single compounds. However, when the syntheses of $RGa(C_5H_4Me)_2$ (R = Me, Et) and $Me_nGa(C_5H_4SiMe_3)_{3-n}$ (n =1, 2) by analogous stoichiometric ligand redistribution reactions were investigated, mixtures of compounds were the isolated products. The heteroleptic organogallium compound $Me_2Ga(C_5H_4Me)$ has also been prepared in high yields by using metathetical reactions between Me_2GaCl and $Li(C_5H_4Me)$ in pentane and between $Cl_2Ga(C_5H_4Me)$, formed in-situ from $Ga(C_5H_4Me)_3$ and $GaCl_3$ in diethyl ether, and LiMe. All pure compounds have been characterized by their physical properties, elemental analyses, NMR spectra, and cryoscopic molecular weight studies.

Introduction

Whether a heteroleptic organogallium compound of the type GaR_2R' exists as a single compound or undergoes a series of ligand redistribution reactions to form a mixture of GaR_2R', GaR'_2R, GaR'_3, and GaR_3 depends on the nature of the organic groups and the phase. When the organic groups are methyl and phenylethnyl as in $Me_2Ga(C{\equiv}CPh)$,[1] a single compound exists in the solid phase and in benzene solution. Both the X-ray structural study of a crystal[1c] and the cryoscopic molecular weight study of a benzene solution[1a] identified the presence of dimers. The structure of the dimer in the solid phase had phenylethnyl groups bridging four coordinate gallium atoms.[1c] In contrast, the characterization data for gallium compounds that contained only methyl and *tert*-butyl groups as in Me_2Ga(t-Bu) were consistent with the existence of mixtures with $GaMe_3$, $MeGa(t\text{-}Bu)_2$, and $Ga(t\text{-}Bu)_3$.[2] When the organic substituents are a methyl or an ethyl group and a cyclopentadienyl group as in $Me_2Ga(C_5H_5)$,[3] $Et_2Ga(C_5H_5)$,[3b,4] and $EtGa(C_5H_5)_2$,[4] single compounds exist in the solid phase, but dissolution in benzene produced equilibrium mixtures of monomeric species including GaR_3, $R_2Ga(C_5H_5)$, $RGa(C_5H_5)_2$, and/or $Ga(C_5H_5)_3$ (R = Me, Et). In contrast, $MeGa(C_5H_5)_2$ [3a] cannot be isolated as a pure compound in any phase. A benzene solution consisted of a mixture of $MeGa(C_5H_5)_2$, $Me_2Ga(C_5H_5)$, and $Ga(C_5H_5)_3$, whereas the product isolated after reacting $Ga(C_5H_5)_3$ and $GaMe_3$ in a 2:1 mol ratio was a mixture of $Me_2Ga(C_5H_5)$ and $Ga(C_5H_5)_3$. X-ray structural studies of $Me_2Ga(C_5H_5)$,[3d] $Et_2Ga(C_5H_5)$,[4] and $EtGa(C_5H_5)_2$ [4] identified polymeric structures with cyclopentadienyl units bridging four-coordinate gallium in each case. Even though these isolable solids are polymers, the parent $Ga(C_5H_5)_3$ is a monomer in the solid state and in benzene solution.[5] In this paper we describe the nature of $Ga(C_5H_4Me)_3$ and $Ga(C_5H_4SiMe_3)_3$ and the effects of these monosubstituted cyclopentadienyl ligands on the chemistry of the heteroleptic organogallium compounds $R_nGa(C_5H_4Me)_{3-n}$ (R = Me, Et; n = 1, 2) and $Me_nGa(C_5H_4SiMe_3)_{3-n}$ (n =1, 2).

Results and Discussion

The cyclopentadienyl derivatives $Ga(C_5H_4Me)_3$ and $Ga(C_5H_4SiMe_3)_3$ were prepared by reacting $GaCl_3$ with $Li(C_5H_4R)$ (R = Me, $SiMe_3$) (eq 1) in diethyl ether. The

$$GaCl_3 + 3\,Li(C_5H_4R) \xrightarrow[0\ °C]{Et_2O} Ga(C_5H_4R)_3 + 3\,LiCl \qquad (1)$$
$$R = Me,\ SiMe_3$$

desired product was separated from the LiCl and excess $Li(C_5H_4R)$ by extraction with pentane. Removal of the pentane by vacuum distillation at room temperature lead to the isolation of $Ga(C_5H_4Me)_3$ as a golden-yellow oil. The trimethylsilyl derivative $Ga(C_5H_4SiMe_3)_3$ was a golden-brown/amber liquid. Even though both com-

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pounds are nonvolatile and decompose slowly at room temperature, they had acceptable elemental analyses for carbon and hydrogen. The original liquids became increasingly viscous and darker in color with time. These observations are consistent with the occurrence of prototropic rearrangements of the substituted cyclopentadienide rings (isomerization) and subsequent Diels−Alder dimerization reactions.[6] Similar conclusions have been made for other heavy group 13 metal cyclopentadienyl derivatives.[5,6−8] The closely related compound $Ga(C_5H_5)_3$ also decomposes/isomerizes at room temperature with a change in color from colorless to yellow.[5] Since $Ga(C_5H_4Me)_3$ and $Ga(C_5H_4SiMe_3)_3$ cannot be distilled or recrystallized, the isolation of analytically pure compounds required the use of high-purity reagents and the minimization of potential side reactions that might produce impurities. Full details of the preparative procedures are described in the Experimental Section.

The ^1H NMR spectrum of $Ga(C_5H_4Me)_3$ exhibited three resonances, one for the ring methyl group and two for the cyclopentadienide ring protons. A fourth line at 5.99 ppm was observed, but it is believed to be due to an impurity of C_5H_5 that probably exists as $Ga(C_5H_4Me)_2(C_5H_5)$. Fractional distillation of the methylcyclopentadiene monomer prior to reaction with the Li(n-Bu) demonstrated that this impurity originated with the commercially available methylcyclopentadiene dimer. Even though this impurity was minimized to the extent that it did not significantly impact the elemental analysis of $Ga(C_5H_4Me)_3$, it could never be eliminated. The literature[7] reveals that the related compound $Al(C_5H_4Me)_3$, a light yellow oil, was also contaminated with an impurity of C_5H_5. The ^{13}C NMR spectrum of $Ga(C_5H_4Me)_3$ had a total of four resonances with one for the methyl group and three for ring carbon atoms. Low-temperature ^1H NMR techniques (−50 °C was the lowest temperature studied) were unable to sufficiently slow the migration of the metal about the cyclopentadienyl ring so that the lines for the individual static structures could be observed. Similar observations have been made for $Ga(C_5H_5)_3$,[5] $In(C_5H_5)_3$,[8] and $In(C_5H_4Me)_3$.[8] Even though the NMR spectra of $Ga(C_5H_4Me)_3$ are consistent with either fluxional or nonfluxional rings to gallium, the compound is believed to have fluxional rings with η^1-bonding. If the compound were nonfluxional and had a "static" structure, the *ipso*-carbon atom of each of the three cyclopentadienyl rings would have to be bonded both to gallium and to a methyl group, a sterically unfavorable structure.

The resonances in the ^1H and ^{13}C NMR spectrum of $Ga(C_5H_4SiMe_3)_3$ have chemical shifts that are as expected for this compound with fluxional cyclopentadienyl rings.[6] However, all lines were considerably broader than those observed for $Ga(C_5H_4Me)_3$. This increased line broadening is related to the variety of sigmatropic rearrangement processes that occur for the molecule, including metallotropic shifts of the gallium fragment, silatropic shifts of the $SiMe_3$ group, and prototropic shifts of ring hydrogen atoms. The rate of the metallotropic shift of the gallium fragment is expected to occur faster than the other rearrangements, as the rate of a sigmatropic rearrangement increases with the metallic character of the migrating group.[6] Thus, the slower movement of the $SiMe_3$ group leads to two resonances, an intense line at 0.24 and a smaller line at −0.12 ppm. These lines may be assigned to the $SiMe_3$ group in different vinyl positions on the cyclopentadienyl ring.

The methyl-substituted cyclopentadienyl gallium compound $Ga(C_5H_4Me)_3$ is a Lewis acid, as it formed 1:1 adducts with NMe_3 and THF. Both adducts were solids at room temperature. The NMe_3 adduct was colorless, whereas the THF adduct was pale yellow. Both adducts were stable to dissociation of the base at room temperature. When sublimation of $Ga(C_5H_4Me)_3\cdot NMe_3$ was attempted, only a small quantity of a colorless solid sublimed at 35 °C. Most of the material did not sublime but became brown, an indication of isomerization.[6] In contrast, when the THF adduct was heated at its melting point of 78−81 °C, no color change was observed. Thus, these adducts have less tendency to decompose and/or isomerize than does $Ga(C_5H_4Me)_3$.

The heteroleptic organogallium compounds $R_2Ga(C_5H_4Me)$ (R = Me, Et) were prepared by stoichiometric ligand redistribution reactions[3a,4] (eq 2) between $Ga(C_5H_4Me)_3$ and $GaMe_3$ or $GaEt_3$, as appropriate. The

$$2\ GaR_3 + Ga(C_5H_4Me)_3 \xrightarrow[25\ °C]{pentane} 3\ R_2Ga(C_5H_4Me) \quad (2)$$

compound $Me_2Ga(C_5H_4Me)$ was isolated by vacuum sublimation at room temperature, whereas $Et_2Ga(C_5H_4Me)$ was a mobile liquid that was purified by vacuum distillation at room temperature. The excellent elemental analysis and the sharp melting point of $Me_2Ga(C_5H_4Me)$ (61.5−62.0 °C) identify the solid as a single compound. Liquid $Et_2Ga(C_5H_4Me)$ was also an analytically pure, single compound at room temperature. The ^1H NMR spectrum of this neat, colorless liquid exhibited one set of sharp lines that are consistent with $Et_2Ga(C_5H_4Me)$. One set of sharp resonances suggests the presence of one species, especially since either multiple sets of lines or line broadening is observed at room temperature when solutions of multiple species are formed by a ligand redistribution reaction (eq 3). The closely related compound $Et_2Ga(C_5H_5)$[4] (mp 35−36 °C) also exists as a single species in the liquid state at 45 °C according to its ^1H NMR spectrum. Conversely, $EtGa(C_5H_5)_2$ exists in the solid state as a pure single compound, but its melt (mp 39.0−39.4 °C) forms multiple species according to its ^1H NMR spectrum at 45 °C.[4] As $Me_2Ga(C_5H_4Me)$ was a crystalline solid at room temperature, an X-ray structural study was attempted. However, the crystals of $Me_2Ga(C_5H_4Me)$ were twinned and unsuitable for study. Crystals could not be obtained from either pentane, methylcyclohexane, or benzene solutions even though the compound was very soluble. It should be noted that $Me_2Ga(C_5H_4Me)$ was more stable toward isomerization than was either $Et_2Ga(C_5H_4Me)$ or $Ga(C_5H_4Me)_3$. Crystals of $Me_2Ga(C_5H_4Me)$ were stored in sealed ampules at room temperature for over one year without any evidence of decomposition/isomerization by ^1H NMR spectroscopy. In contrast, samples of liquid $Et_2Ga(C_5H_4Me)$ in sealed ampules gradually changed color and became yellow-green and increasingly viscous with time at room temperature.

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Cryoscopic molecular weight studies of benzene solutions of $Me_2Ga(C_5H_4Me)$ identified the presence of monomeric species. ^1H NMR spectral studies of solutions of $Me_2Ga(C_5H_4Me)$ in d_8-THF, d_6-benzene, d_8-toluene, d_{12}-cyclohexane, $CDCl_3$, and CD_2Cl_2 revealed that $Me_2Ga(C_5H_4Me)$ does not exist as a single compound in solution but forms an equilibrium mixture of $Me_2Ga(C_5H_4Me)$, $MeGa(C_5H_4Me)_2$, and $GaMe_3$ (eq 3).

$$2\ R_2Ga(C_5H_4Me) \underset{K}{\overset{\text{solvent}}{\rightleftharpoons}} GaR_3 + RGa(C_5H_4Me)_2 \quad (3)$$

The presence of multiple species at the normal operating temperature of the instrument was evident from the multiple gallium−methyl lines. When the solvent was d_8-THF, three sharp resonances were observed in the gallium−methyl region of the spectrum, whereas two sets of lines were observed for the protons of the C_5H_4-Me group. This multiplicity of lines is consistent with slow exchange between the species in eq 3. When the solvent was not a Lewis base, exchange was faster. Two broad lines were observed for the methyl groups bonded to gallium, and the C_5H_4Me group exhibited only one set of lines. The identity of the ^1H NMR lines was confirmed by comparing the observed spectrum with the spectrum recorded for a mixture of $Ga(C_5H_4Me)_3$ and $GaMe_3$ in a 1:1 mol ratio as well as with the spectra for pure $GaMe_3$ and $Ga(C_5H_4Me)_3$ in the same solvent. The equilibrium constant for the redistribution of $Me_2Ga(C_5H_4Me)$ in THF solution (eq 3) was estimated to be 2.3×10^{-2} by using the integration data from the ^1H NMR spectra at the normal operating temperature of the instrument. The corresponding equilibrium constant for $Me_2Ga(C_5H_5)$ was 1.4×10^{-1}.[3a]

The solution chemistry of $Et_2Ga(C_5H_4Me)$ paralleled that of $Me_2Ga(C_5H_4Me)$. A cryoscopic molecular weight study demonstrated the presence of monomeric species in benzene solution, whereas ^1H NMR spectral studies identified multiple species formed by a ligand redistribution reaction (eq 3). Multiple sets of gallium−ethyl lines were observed for each of the solvents including d_8-THF, C_6D_6, C_6D_{12}, and d_8-toluene. When d_8-THF was the solvent, the spectrum displayed three sharp triplets and three quartets for the ethyl group protons, one for each of the three species in the equilibrium (eq 3), $GaEt_3$, $Et_2Ga(C_5H_4Me)$, and $EtGa(C_5H_4Me)_2$. In addition, two sets of resonances were observed for the C_5H_4-Me ring protons, as observed for $Me_2Ga(C_5H_4Me)$. When the solvent was not basic, such as C_6D_6, C_6D_{12}, and d_8-toluene, broad singlets were observed in place of the expected triplets and/or quartets due to more rapid ethyl group exchange. The NMR spectrum of a d_8-toluene solution at −40 °C displayed only broadening of the lines for the ethyl groups and a single set of lines for the C_5H_4-Me ring. Thus, the rate of the metallotropic shift remained sufficiently rapid that lines for the static structure of the C_5H_4Me ring were not observed.[6] The equilibrium constant for the redistribution reaction (eq 3) in THF at ambient temperature, as calculated by using the integration values for the methyl, methylene, and cyclopentadienide ring protons, had a value of 1.5×10^{-2}. The equilibrium constant for the redistribution of $Et_2Ga(C_5H_5)$[4] as calculated from the ^1H NMR spectral data for eq 3 was 1.3×10^{-2}.

Ligand redistribution reactions (eq 4) were used for the attempted synthesis of the monoalkyl derivatives $MeGa(C_5H_4Me)_2$ and $EtGa(C_5H_4Me)_2$, but neither could be isolated as a single compound. Removal of solvent

$$GaR_3 + 2\ Ga(C_5H_4Me)_3 \xrightarrow[25\ ^\circ C]{\text{pentane}} 3\ RGa(C_5H_4Me)_2 \quad (4)$$

resulted in the isolation of a liquid at room temperature in each case. Vacuum distillation of the resulting liquid at room temperature separated a distillate from a yellow-brown liquid residue. ^1H NMR spectral studies of benzene solutions identified the distillate as mixture of $RGa(C_5H_4Me)_2$ and $R_2Ga(C_5H_4Me)$ (R = Me, Et) and the yellow-brown residue as $Ga(C_5H_4Me)_3$ with a small amount of $RGa(C_5H_4Me)_2$. Thus, the chemistry of $RGa(C_5H_4Me)_2$ (R = Me, Et) is similar to that of $MeGa(C_5H_5)_2$,[3a] as none of these compounds can be isolated as pure single compounds. In contrast, $EtGa(C_5H_5)_2$[4] is the only dicyclopentadienyl derivative that has been isolated as a pure single compound, and it has a polymeric structure in the solid phase.

A comparison of the ^1H NMR spectra of solutions of GaR_3 (R = Me, Et) and $Ga(C_5H_4Me)_3$ mixed in 2:1 and 1:1 mol ratios in benzene with the spectra of the products isolated from the reaction designed to prepare $RGa(C_5H_4Me)_2$ (eq 4) demonstrated that the isolated products were mixtures and not originally pure compounds that were undergoing ligand redistribution reactions (eq 5) when placed in solution. When the

$$2\ RGa(C_5H_4Me)_2 \underset{K}{\overset{\text{solvent}}{\rightleftharpoons}} R_2Ga(C_5H_4Me) + Ga(C_5H_4Me)_3 \quad (5)$$

reagents were mixed in the stoichiometric ratio of 1:2 mol in C_6D_6, the resulting ^1H NMR spectrum had relative integrations of lines for the R group to the methyl line for the C_5H_4Me group that were consistent with the formula $RGa(C_5H_4Me)_2$, whereas the spectra for the isolated products did not. Second, the spectrum for the stoichiometric mixture had sharper lines than those observed in the spectra of either $Me_2Ga(C_5H_4Me)$ or $Et_2Ga(C_5H_4Me)$. Thus, the ethyl derivative displayed the expected triplet/quartet signals. Signal averaging for the C_5H_4Me group lines in the spectra of samples dissolved in C_6D_6 resulted in only one set of lines. The d_8-THF spectra once again showed a reduction in the rate of ligand exchange, as separate sets of lines were observed for the multiple C_5H_4Me groups and alkyl groups in the multiple species.

Ligand redistribution reactions between $Ga(C_5H_4SiMe_3)_3$ and $GaMe_3$ were investigated as potential routes to $Me_2Ga(C_5H_4SiMe_3)$ and $MeGa(C_5H_4SiMe_3)_2$, but neither could be isolated as single compounds according to the ^1H NMR spectral data. Instead, mixtures were formed by ligand redistribution reactions of the intended products (eqs 3 and 5). The additional fluxionality of the $SiMe_3$ group combined with the metallotropic shifts of the gallium probably hinders the formation of the cyclopentadienyl bridge, which appears necessary to stabilize these types of compounds in the condensed state and make them isolable as single compounds. The steric bulk of the $SiMe_3$ group might also be a factor to prevent bridging.

The compound $Me_2Ga(C_5H_4Me)$ has also been prepared in ∼85% yield by using a metathetical reaction between Me_2GaCl[11] and excess $Li(C_5H_4Me)$ in pentane solution (eq 6). The product isolated after removal of

$$Me_2GaCl + Li(C_5H_4Me) \xrightarrow[25\ °C]{pentane} Me_2Ga(C_5H_4Me) + LiCl \quad (6)$$

solvent and subsequent sublimation at room temperature had excellent elemental analyses for C, H, and Ga and a sharp melting point. All characterization data were in agreement with those observed for the compound prepared by the ligand redistribution reaction. The synthesis of $Me_2Ga(C_5H_4Me)$ by a metathetical reaction is significant because the first reported synthesis of $Me_2Ga(C_5H_5)$ by a metathetical reaction in cyclohexane gave a low yield (30−60%) of an impure product.[3b,c] This original product had an unsatisfactory elemental analysis, and its melting point was significantly lower than that observed for the pure compound prepared by a ligand redistribution reaction.[3a] The difference between the results of the syntheses of $Me_2Ga(C_5H_4Me)$ and of $Me_2Ga(C_5H_5)$[3b,c] by metathetical reactions may be attributed to the solubility of these compounds in the reaction solvent. The product $Me_2Ga(C_5H_4Me)$ is soluble in pentane, whereas $Me_2Ga(C_5H_5)$[3a] is insoluble in cyclohexane. Thus, the reaction between Me_2GaCl and an excess of $Li(C_5H_5)$ in cyclohexane was probably incomplete, and samples of $Me_2Ga(C_5H_5)$ might have been contaminated with Me_2GaCl, a compound with volatility similar to $Me_2Ga(C_5H_5)$.

The third route to $Me_2Ga(C_5H_4Me)$ in high yield involved a metathetical reaction between $Cl_2Ga(C_5H_4Me)$ and LiMe in diethyl ether solution (eq 7). The chloro

$$2\ GaCl_3 + Ga(C_5H_4Me)_3 + 2\ LiMe \xrightarrow[0\ °C]{Et_2O} 3\ Me_2Ga(C_5H_4Me) + 2\ LiCl \quad (7)$$

derivative $Cl_2Ga(C_5H_4Me)$ was formed in-situ by using a stoichiometric ligand redistribution reaction between $Ga(C_5H_4Me)_3$ and $GaCl_3$. Extensive research on these chlorogallium methylcyclopentadienyl derivatives has revealed that $Cl_2Ga(C_5H_4Me)$ and $ClGa(C_5H_4Me)_2$ cannot be isolated and characterized because of the occurrence of facile isomerization/polymerization reactions. If $Cl_2Ga(C_5H_4Me)$ and $ClGa(C_5H_4Me)_2$ are to be used as reagents, best results are obtained if they are reacted soon after formation in solvents that are Lewis bases, diethyl ether, or THF.

Five heteroleptic diorganogallium and -indium cyclopentadienyl derivatives, $Me_2Ga(C_5H_5)$,[3a] $Et_2Ga(C_5H_5)$,[4] $Me_2Ga(C_5H_4Me)$, $Et_2Ga(C_5H_4Me)$, and $Me_2In(C_5H_5)$,[9] but only one dicyclopentadienyl derivative, $EtGa(C_5H_5)_2$,[4] have been prepared and isolated as analytically pure single compounds in the condensed phase at room temperature. However, when these compounds are dissolved, equilibrium mixtures of multiple species are formed by ligand redistribution reactions.[3a,4] All solids that have been characterized by X-ray structural studies exist as linear polymers with the cyclopentadienyl groups bridging four-coordinate MR_2 moieties.[3d,4,8,9] In contrast, solutions are composed of monomers according to cryoscopic molecular weight studies.[3,4] Thus, four-coordinate metal centers formed by bridging cyclopentadienyl groups are necessary for the stabilization of a compound in the condensed phase, whereas the presence of monomers permits facile ligand redistribution reactions to form multiple species. As $Me_2Ga(C_5H_4Me)$ and $Et_2Ga(C_5H_4Me)$ exist as single compounds in the condensed state, they probably exist as polymers. The only dicyclopentadienyl derivative that has been isolated as a single pure compound is $EtGa(C_5H_5)_2$, [4] and its isolation required shifting the ligand redistribution equilibrium to minimize the presence of $Et_2Ga(C_5H_5)$ in the solution prior to removal of solvent and isolation of the compound by sublimation. When the equilibrium had not been shifted, removal of solvent and subsequent sublimation produced a product with low carbon/hydrogen analyses, probably a mixture of $EtGa(C_5H_5)_2$ and $Et_2Ga(C_5H_5)$. Since $Et_2Ga(C_5H_5)$ has weaker London dispersion forces and is more volatile than $EtGa(C_5H_5)_2$, $Et_2Ga(C_5H_5)$ sublimed before or with $EtGa(C_5H_5)_2$ contaminated the desired product and produced low carbon and hydrogen analysis. Thus, $EtGa(C_5H_5)_2$ is the only example of a gallium or indium dicyclopentadienyl derivative, to date, that has the appropriate magnitude of the equilibrium constant for the redistribution equilibrium, has sufficiently strong bridges to stabilize the condensed phase with four-coordinate gallium and overcome the loss of entropy due to forming the polymer, but has sufficiently weak London dispersion forces and weak bridges to permit sublimation/distillation prior to decomposition. In the case of the other gallium or indium dicyclopentadienide derivatives that have been investigated, two cyclopentadienide groups prevent formation of the bridge necessary for stabilization.

Experimental Section

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. The reagent $Li(C_5H_4Me)$ was prepared by adding a solution of Li(n-Bu) in hexane/pentane to an excess of fractionally distilled C_5H_5Me at 0 °C. The insoluble product was washed three times with the reaction solvent and then thoroughly dried under vacuum. The trimethylsilyl derivative $Li(C_5H_4SiMe_3)$ was prepared by the literature method.[10] The compound Me_2GaCl[11a,b] was prepared by a ligand redistribution reaction between $GaMe_3$ and $GaCl_3$ in pentane at room temperature.[11c] 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 neat liquids or Nujol mulls between CsI plates were recorded by using a Perkin-Elmer 683 spectrometer. ^1H NMR (400 MHz) and ^{13}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 C_6D_5H at δ 7.15 or the residual proton in the other deuterated solvents, as appropriate. Carbon-13 chemical shifts are refer-

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enced 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 Drezdzon.[12]

Synthesis of $Ga(C_5H_4Me)_3$. A Solv-Seal flask, charged with 6.31 g of $Li(C_5H_4Me)$ (73.4 mmol) and approximately 125 mL of diethyl ether, was connected to a sidearm dumper that contained 4.07 g of freshly sublimed $GaCl_3$ (23.1 mmol) dissolved in approximately 50 mL of ether. After the $Li(C_5H_4Me)/Et_2O$ slurry was cooled to 0 °C, the $GaCl_3/Et_2O$ solution was slowly added over a period of 1 h. The resulting mixture was stirred overnight while warming to room temperature. The Et_2O was then removed by vacuum distillation, and approximately 50 mL of pentane was added to the two-necked Schlenk flask. The product, $Ga(C_5H_4Me)_3$, was isolated by three extractions. The remaining LiCl was a colorless solid. The pentane was then removed from the apparatus by vacuum distillation followed by overnight pumping to leave 6.15 g (20.0 mmol, 86.7% yield, based on $GaCl_3$) of a pale golden-yellow liquid. Since $Ga(C_5H_4Me)_3$ decomposes slowly at room temperature as demonstrated by the original liquid becoming increasingly viscous and darker in color with time, it was stored under vacuum in sealed ampules at −20 °C. $Ga(C_5H_4Me)_3$: ^1H NMR (C_6D_6, δ) 5.99 (s, 0.2, C_5H_5, see Discussion), 5.82 (s, 4.2, ring-*H*), 5.46 (s, 4.6, ring-*H*), 2.08 (s, 9.0, ring-CH_3); (d_8-THF, δ): 5.95 (s, 4.6, ring-*H*), 5.85 (s, 0.2, C_5H_5), 5.01 (s, 5.1, ring-*H*), 2.08 (s, 9.0, ring-CH_3); (neat liquid, capillary of C_6D_6 for reference, δ): 5.79 (s, 0.2, C_5H_5), 5.58 (s, 6.5, ring-*H*), 5.22 (s, 6.5, ring-*H*), 1.95 (s, 9.0, ring-CH_3); ^{13}C NMR (C_6D_6, δ) 139.56 (s, ring-*C*), 114.26 (s, ring-*C*), 112.72 (s, $-C_5H_5$), 103.05 (s, ring-*C*), 15.53 (s, $-CH_3$). Anal. Calcd for $C_{18}H_{21}Ga$: C, 70.40; H, 6.90. Found: C, 69.97; H, 6.88. Cryoscopic molecular weight, benzene solution, fw 307.08 (molality, obsd mol wt, assoc): 0.0868, 343, 1.12; 0.0695, 345, 1.12; 0.0458, 356, 1.16.

Synthesis of $Ga(C_5H_4SiMe_3)_3$. The synthesis of $Ga(C_5H_4SiMe_3)_3$ was identical to that previously described for $Ga(C_5H_4Me)_3$. A diethyl ether solution of $GaCl_3$ (3.53 g, 20.1 mmol) was added to an ether slurry of $Li(C_5H_4SiMe_3)$ (8.73 g, 60.5 mmol) at −78 °C over a 30 min period. The reaction mixture was stirred overnight at −78 °C, and the Et_2O was removed by vacuum distillation. The product $Ga(C_5H_4SiMe_3)_3$ was isolated by three extractions with 50 mL of pentane. The pentane was then removed by vacuum distillation. Overnight pumping at −78 °C left 7.77 g (16.1 mmol, 80.3% yield based on $GaCl_3$) of $Ga(C_5H_4SiMe_3)_3$ as a golden-brown liquid. $Ga(C_5H_4SiMe_3)_3$: ^1H NMR (C_6D_6, δ) 6.25 (s br, 5.2, ring-*H*), 5.96 (s, 1.4, C_5H_5, see Discussion), 5.76 (s br, 52.3, ring-*H*), 0.24 (s, 27, Si*Me*$_3$), −0.12 (s, 1.0, Si*Me*$_3$); ^{13}C NMR (C_6D_6, δ) 120.19 (br, ring-*C*), 113.45 (br, ring-*C*), 108.12 (br, ring-*C*), 1.74 (Si*Me*$_3$), 0.42 (Si*Me*$_3$), −1.68 (Si*Me*$_3$). Soluble in pentane, ether, and benzene. Anal. Calcd for $C_{24}H_{39}GaSi_3$: C, 59.86; H, 8.16. Found: C, 60.10; H, 7.22.

Synthesis of Lewis Adducts of $Ga(C_5H_4Me)_3$. (a) NMe_3. The Lewis acid $Ga(C_5H_4Me)_3$ (1.402 g, 4.565 mmol) was combined with NMe_3 (0.371 g, 6.28 mmol) in approximately 30 mL of pentane to form a slightly soluble yellow solid at room temperature. The yellow solid was separated by extraction with pentane (four times) to leave a small amount of an unknown insoluble tan solid. The yellow solid was sublimed at 35 °C to a −78 °C coldfinger to give $Ga(C_5H_4Me)_3 \cdot NMe_3$ as a colorless solid. A brown solid remained at the bottom of the sublimator. Prolonged heating of colorless $Ga(C_5H_4Me)_3 \cdot NMe_3$ at 50 °C produced a brown solid that appeared identical to the unsublimed material. $Ga(C_5H_4Me)_3 \cdot NMe_3$: mp 72−73 °C melts with decomposition to a brown liquid; ^1H NMR (C_6D_6, δ) 6.37 (s, 5.1, ring-*H*), 6.13 (s, 0.3, C_5H_5), 5.19 (s, 5.7, ring-*H*), 2.24 (t, 9.0, ring-CH_3), 1.57 (s, 9.6, N−CH_3). Anal. Calcd for $C_{21}H_{30}GaN$: C, 68.88; H, 8.26. Found: C, 68.39; H, 8.04.

(b) THF. A solution of 0.631 g of $Ga(C_5H_4Me)_3$ (2.06 mmol) in THF (approximately 10 mL) was stirred for 2 h. Then the excess THF was removed from the resulting yellow solution by vacuum distillation to afford $Ga(C_5H_4Me)_3 \cdot THF$ (0.668 g, 1.76 mmol, 85.6% yield) as a pale yellow solid. $Ga(C_5H_4Me)_3 \cdot THF$: mp 78−81 °C; ^1H NMR (C_6D_6, δ) 6.06 (s, 0.2, C_5H_5), 5.99 (s, 4.0, ring-*H*), 5.39 (s, 4.9, ring-*H*), 3.46 (m, 3.9, THF), 2.15 (s, 9.0, CH_3), 1.28 (m, 3.2, THF).

Synthesis of $Me_2Ga(C_5H_4Me)$ by a Ligand Redistribution Reaction. A flask containing $Ga(C_5H_4Me)_3$ (0.476 g, 1.55 mmol) was connected to a 90° elbow and a Schlenk flask. Then, 0.361 g of $GaMe_3$ (3.14 mmol) and 25 mL of pentane were vacuum distilled onto the $Ga(C_5H_4Me)_3$ and the solution was allowed to stir overnight at room temperature. Removal of the pentane by vacuum distillation produced a colorless solid that was transferred by vacuum sublimation at room temperature to the attached Schlenk flask held at −196 °C and identified as $Me_2Ga(C_5H_4Me)$ (0.700 g, 3.91 mmol, 84.1% yield based on $Ga(C_5H_4Me)_3$). Large colorless, hexagonal shaped crystalline plates were obtained by heating a sample under vacuum in a sealed tube at 35 °C. The crystals were twinned and were unsuitable for an X-ray structural study. Attempts to grow X-ray quality crystals of $Me_2Ga(C_5H_4Me)$ by recrystallization from pentane, methylcyclohexane, and toluene solutions were unsuccessful. $Me_2Ga(C_5H_4Me)$: mp 61.5−62 °C; ^1H NMR (C_6D_6, δ) 5.98 (s, 1.1, ring-*H*), 5.80 (s, 1.1, ring-*H*), 2.11 (s, 3.0, ring-CH_3), −0.43 (s br, 4.8, *Me*$_3$Ga/*Me*$_2$GaCp), −1.04 (s br, 0.3, *Me*GaCp$_2$); (d_8-THF, δ): 5.84 (s, 0.3, MeGaCp$_2$ ring-*H*), 5.75 (s, 0.9, Me$_2$GaCp ring-*H*), 5.52 (s, 1.0, Me$_2$GaCp ring-*H*), 5.40 (s, 0.3, Me$_2$GaCp ring-*H*), 2.06 (s, 3.0, ring-CH_3), −0.49 (s, 0.9, *Me*$_3$Ga), −0.65 (s, 4.1, *Me*$_2$GaCp), −1.08 (s, 0.3, *Me*GaCp$_2$). Anal. Calcd for $C_8H_{13}Ga$: C, 53.71; H, 7.32. Found: C, 53.91; H, 7.48. Cryoscopic molecular weight, benzene solution, fw 178.91 (molality, obsd mol wt, assoc): 0.0711, 189, 1.06; 0.0578, 190, 1.06; 0.0400, 198, 1.10.

Synthesis of $Me_2Ga(C_5H_4Me)$ by a Metathetical Reaction. A pentane solution of Me_2GaCl[11c] (1.15 g, 8.54 mmol) was combined with 0.755 g of $Li(C_5H_4Me)$ (8.77 mmol) in 25 mL of pentane at 0 °C and stirred overnight. The pentane was removed by vacuum distillation to leave a colorless solid. Sublimation of the resulting solid at room temperature under static vacuum to a Schlenk flask maintained at −196 °C produced $Me_2Ga(C_5H_4Me)$ (1.29 g, 7.20 mmol, 84.4% yield based on Me_2GaCl) as a colorless crystalline solid. The product tested negative for chloride ion (addition of Ag^+ to a hydrolyzed solution). Colorless crystals of $Me_2Ga(C_5H_4Me)$ were grown by sublimation at 35 °C in a sealed and evacuated tube placed at a 45° angle over a drying oven, but they proved unsuitable for an X-ray structural study. $Me_2Ga(C_5H_4Me)$: mp (sublimed solid) 60−62 °C; (crystals) 62−63.5 °C. All spectral data were identical to that previously described for the compound prepared by a ligand redistribution reaction. Anal. Calcd for $C_8H_{13}Ga$: C, 53.71; H, 7.32; Ga, 38.97. Found (sublimed solid): C, 53.42; H, 7.46. Found (crystals): C, 53.49; H, 7.49; Ga, 39.24.

Synthesis of $Me_2Ga(C_5H_4Me)$ from $Ga(C_5H_4Me)_3$, $GaCl_3$, and LiMe. Two tubes with one containing 0.899 g (5.10 mmol) of $GaCl_3$ dissolved in 10 mL of Et_2O and the second containing 11.0 mL of a solution of LiMe in OEt_2 (1.4 M, 15.4 mmol) were attached to a round-bottomed flask charged with 0.785 g (2.56 mmol) of $Ga(C_5H_4Me)_3$ dissolved in 25 mL of Et_2O. First, the colorless $GaCl_3/Et_2O$ solution was added to the pale yellow $Ga(C_5H_4Me)_3/Et_2O$ solution at 0 °C. After the resulting solution was allowed to stir for 30 min, the $LiMe/Et_2O$ solution was added. A colorless precipitate formed immediately. This mixture was warmed to room temperature and stirred overnight. The ether was removed by vacuum distillation while holding the reaction flask at 0 °C until the pressure of the volatile components in the flask at room temperature was less than 2

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(12) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; Wiley: New York, 1968; p 38.

mmHg. Then, a colorless solid was sublimed at room temperature from the reaction flask through an elbow into an attached Schlenk flask maintained at −196 °C. If the vapor pressure of the sublimed solid at room temperature was measurable, i.e., greater than about 2 mm, the volatile material (ether) was removed by vacuum distillation and discarded. The sublimed, colorless solid was identified as $Me_2Ga(C_5H_4Me)$ (0.970 g, 5.42 mmol, 70.9% based on $GaCl_3$) by its melting point and ^1H NMR spectrum. The nonvolatile off-white solid, presumably LiCl, that remained in the reaction flask weighed 0.8542 g. Thus, 90% of the mass of the starting materials was accounted for by the masses of $Me_2Ga(C_5H_4Me)$ and the insoluble solid (LiCl). $Me_2Ga(C_5H_4Me)$: mp 58−61.5 °C. All spectral data were identical to that previously described for the compound prepared by a ligand redistribution reaction.

Attempted Synthesis of $MeGa(C_5H_4Me)_2$ by Ligand Redistribution Reaction. The reagents 0.850 g of $Ga(C_5H_4Me)_3$ (2.77 mmol) and 0.155 g of $GaMe_3$ (1.35 mmol) were combined in approximately 25 mL of pentane and allowed to stir overnight at room temperature. The pentane was then removed by vacuum distillation to leave a yellow-brown liquid, from which a colorless liquid was transferred by vacuum distillation at ambient temperature to an attached Schlenk flask. A yellow-brown liquid remained in the original round-bottomed flask. ^1H NMR spectra identified the distillate as a mixture of $MeGa(C_5H_4Me)_2$ and $Me_2Ga(C_5H_4Me)$, whereas the yellow-brown liquid was found to be predominantly $Ga(C_5H_4Me)_3$ with a trace of $MeGa(C_5H_4Me)_2$. Similar results were obtained when the mol ratio of $Ga(C_5H_4Me)_3$ to $GaMe_3$ was increased to 2.8:1. Colorless liquid distillate: ^1H NMR (C_6D_6, δ) 5.97 (m, 2.2, ring-*H*), 5.375 (t, 2.3, ring-*H*), 2.09 (s, 6.0, ring −CH_3), −0.44 (s, 4.8, *Me*$_2$GaCp), −1.04 (s, 1.4, *Me*GaCp$_2$); (d_8-THF, δ): 5.84 (s, 1.2, MeGaCp$_2$ ring-*H*), 5.75 (s, 1.3, Me$_2$GaCp ring-*H*), 5.52 (s, 1.4, Me$_2$GaCp ring-*H*), 5.40 (s, 1.3, MeGaCp$_2$ ring-*H*), 2.06 (s, 6.0, ring-CH_3), −0.49 (s, 0.6, Ga*Me*$_3$), −0.65 (s, 5.4, *Me*$_2$GaCp), −1.08 (s, 1.3, *Me*GaCp$_2$). Yellow-brown residue: ^1H NMR (C_6D_6, δ) 5.85 (s, 3.2, ring-*H*), 5.51 (s, 3.3, ring-*H*), 2.08 (s, 6.0, ring-CH_3), −1.04 (s, 0.3, *Me*GaCp$_2$).

^1H NMR Spectral Study of $GaMe_3$ and $Ga(C_5H_4Me)_3$ in a 1:2 mol Ratio. An NMR tube was attached to a very small reaction vessel that contained 0.128 g of $Ga(C_5H_4Me)_3$ (0.418 mmol). Then C_6D_6 followed by 0.0242 g of $GaMe_3$ (0.211 mmol) was added by vacuum distillation. The resulting solution was stirred and then poured into the NMR tube. The NMR tube was flame sealed. A second solution with d_8-THF as solvent was prepared by using the identical procedure. ^1H NMR (C_6D_6, δ): 5.95 (s, 3.4, ring-*H*), 5.69 (s, 3.4, ring-*H*), 2.08 (s, 6.0, ring-CH_3), −0.44 (s, 1.1, *Me*$_2$GaCp), −1.05 (s, 1.9, *Me*GaCp$_2$); (d_8-THF): 5.94 (s, 0.9, GaCp$_3$ ring-*H*), 5.83 (s, 2.1, MeGaCp$_2$ ring-*H*), 5.75 (s, −, Me$_2$GaCp ring-*H*), 5.52 (s, −, Me$_2$GaCp ring-*H*), 5.39 (s, 2.2, MeGaCp$_2$ ring-*H*), 5.01 (s, 0.7, GaCp$_3$ ring-*H*), 2.06 (s, 6.0, ring-CH_3), −0.50 (s, −, Ga*Me*$_3$), −0.65 (s, 0.4, *Me*$_2$GaCp), −1.08 (s, 1.5, *Me*GaCp$_2$).

^1H NMR Spectral Study of $GaMe_3$ and $Ga(C_5H_4Me)_3$ in a 1:1 mol Ratio. An NMR tube was attached to a small reaction vessel that contained 0.0847 g of $Ga(C_5H_4Me)_3$ (0.276 mmol). The solvent, d_8-THF, followed by 0.0327 g of $GaMe_3$ (0.285 mmol) was added by vacuum distillation. The resulting solution was stirred and poured into the NMR tube. The tube was flame sealed. ^1H NMR (d_8-THF, δ): 5.83 (s, 2.3, MeGaCp$_2$ ring-*H*), 5.74 (s, 1.6, Me$_2$GaCp ring-*H*), 5.51 (s, 1.8, Me$_2$GaCp ring-*H*), 5.39 (s, 2.6, MeGaCp$_2$ ring-*H*), 2.06 (s, 4.5, ring-CH_3), −0.50 (s, 0.3, Ga*Me*$_3$), −0.65 (s, 6.2, *Me*$_2$GaCp), −1.08 (s, 2.3, *Me*GaCp$_2$).

Synthesis of $Et_2Ga(C_5H_4Me)$ by Ligand Redistribution Reaction. A solution that was prepared on the vacuum line by combining 0.549 g of $Ga(C_5H_4Me)_3$ (1.79 mmol), 0.588 g of $GaEt_3$ (3.75 mmol), and approximately 25 mL of pentane was allowed to stir overnight. The pentane was removed by vacuum distillation to leave a yellow-green liquid. Vacuum distillation of this yellow-green liquid with a short path still afforded pure $Et_2Ga(C_5H_4Me)$ as a colorless liquid (1.04 g, 5.00 mmol, 93.1% yield based on $Ga(C_5H_4Me)_3$). Samples were stored in sealed ampules at −20 °C. $Et_2Ga(C_5H_4Me)$: colorless liquid at ambient temperature; ^1H NMR (C_6D_6, δ) 6.07 (s, 1.3, ring-*H*), 5.90 (t, 1.3, ring-*H*), 2.15 (s, 3.0, ring-CH_3), 1.02 (s br, 5.2, Et$_3$Ga/Et$_2$GaCp-CH_3), 0.82 (t, 0.2, EtGaCp$_2$−CH_3), 0.21 (s br, 3.5, Et$_3$Ga/Et$_2$GaCp-CH_2), −0.20 (q, 0.1, EtGaCp$_2$−CH_2); (d_8-THF, δ): 5.92 (s, 0.2, EtGaCp$_2$ ring-*H*), 5.87 (s, 1.1, Et$_2$GaCp ring-*H*), 5.52 (s, 1.2, Et$_2$GaCp ring-*H*), 5.34 (s, 0.2 EtGaCp$_2$ ring-*H*), 2.08 (s, 3.0, ring-CH_3), 1.07 (t, 1.4, GaEt$_3$−CH_3), 0.99 (t, 4.5, Et$_2$GaCp-CH_3), 0.84 (t, 0.3, EtGaCp$_2$−CH_3), 0.27 (q, 1.0, GaEt$_3$−CH_2), 0.12 (q, 3.3, Et$_2$GaCp-CH_2), −0.13 (q, 0.1, EtGaCp$_2$−CH_2); (neat liquid, capillary of C_6D_6 for reference, δ): 6.14 (s, 0.04, −C_5H_5), 5.85 (s, 2.1, ring-*H*), 5.80 (s, 2.1, ring-*H*), 2.10 (s, 3.0, ring-CH_3), 0.94 (t, $J_{HH} = 8.0$ Hz, 7.1, Et$_2$GaCp−CH_3), 0.05 (q, $J_{HH} = 8.0$ Hz, 4.3, Et$_2$GaCp−CH_2); ^{13}C NMR (C_6D_6, δ) 139.14 (s, ring-*C*), 112.35 (s, ring-*C*), 103.54 (s, ring-*C*), 15.71 (s, ring-*Me*), 10.72 (s, Et$_2$GaCp−*C*H$_2$), 6.38 (s, Et$_2$GaCp−*C*H$_3$). Anal. Calcd for $C_{10}H_{17}Ga$: C, 58.04; H, 8.28. Found: C, 58.11; H, 8.13. Cryoscopic molecular weight, benzene solution, fw 206.96 (molality, obsd mol wt, assoc): 0.0825, 177, 0.85; 0.0593, 173, 0.84; 0.0383, 167, 0.81.

Attempted Synthesis of $EtGa(C_5H_4Me)_2$ by Ligand Redistribution Reaction. A solution prepared from $Ga(C_5H_4Me)_3$ (0.922 g, 3.00 mmol), $GaEt_3$ (0.210 g, 1.34 mmol), and 25 mL of pentane was allowed to stir overnight at room temperature. Then the pentane was removed by vacuum distillation to leave a yellow liquid, which was vacuum distilled at room temperature. A yellow-green liquid distilled through a 90° elbow attached to a Schlenk flask held at −196 °C, whereas a yellow-brown liquid remained in the original reaction flask. ^1H NMR spectroscopy identified the yellow-brown liquid as predominantly $Ga(C_5H_4Me)_3$ with a trace of $EtGa(C_5H_4Me)_2$, while the distilled liquid was identified as a mixture of $Et(C_5H_4Me)_2$ and $Et_2Ga(C_5H_4Me)$. Yellow-brown liquid: ^1H NMR (C_6D_6, δ) 5.84 (s, 2.6, ring-*H*), 5.49 (s, 3.0, ring-*H*), 2.08 (s, 6.0, ring-CH_3), 0.83 (t, 0.4, EtGaCp$_2$−CH_3), −0.20 (q, 0.1, EtGaCp$_2$−CH_2). Yellow-green distilled liquid: ^1H NMR (C_6D_6, δ) 6.01 (s, 2.4, ring-*H*), 5.77 (t, 2.6, ring-*H*), 2.12 (s, 6.0, ring-CH_3), 1.02 (t, 3.5, Et$_2$GaCp-CH$_3$), 0.82 (t, 2.2, EtGaCp$_2$−CH_3), 0.22 (q, 2.5, Et$_2$GaCp-CH_2), −0.21 (q, 1.4, EtGaCp$_2$−CH_2).

^1H NMR Spectral Study of $GaEt_3$ and $Ga(C_5H_4Me)_3$ in a 1:2 mol Ratio. An NMR tube was attached to a small reaction vessel that contained 0.128 g of $Ga(C_5H_4Me)_3$ (0.417 mmol). After the solvent C_6D_6 was added by vacuum distillation, 0.0334 g of $GaMe_3$ (0.213 mmol) was distilled into the vessel. The resulting solution was warmed from −196 °C to room temperature, stirred, and then poured into the NMR tube. The NMR tube was flame sealed. An identical procedure was carried out with d_8-THF as solvent. The ^1H NMR spectra were indicative of an equilibrium mixture of species formed by a ligand redistribution reaction. ^1H NMR (C_6D_6, δ): 5.98 (s, 2.4, ring-*H*), 5.70 (s, 2.5, ring-*H*), 2.11 (s, 6.0, ring-CH_3), 1.02 (t, 0.8, Et$_2$GaCp−CH_3), 0.83 (t, 2.6, EtGaCp$_2$−CH_3), 0.22 (q, 0.6, Et$_2$GaCp−CH_2), −0.21 (q, 1.8, EtGaCp$_2$−CH_2); (d_8-THF): 5.94 (s, 1.3, GaCp$_3$ ring-*H*), 5.92 (s, 1.5, EtGaCp$_2$ ring-*H*), 5.87 (s, 0.4, Et$_2$GaCp ring-*H*), 5.52 (s, 0.4, Et$_2$GaCp ring-*H*), 5.34 (s, 1.3 EtGaCp$_2$ ring-*H*), 5.01 (s, 1.6, GaCp$_3$ ring-*H*), 2.08 (s, 6.0, ring-CH_3), 0.99 (t, 1.4, Et$_2$GaCp−CH_3), 0.84 (t, 1.0, EtGaCp$_2$−CH_3), 0.11 (q, 1.0, Et$_2$GaCp−CH_2), −0.14 (q, 1.7, EtGaCp$_2$−CH_2).

Attempted Synthesis of $Me_2Ga(C_5H_4SiMe_3)$ by a Ligand Redistribution Reaction. After a solution of $Ga(C_5H_4SiMe_3)_3$ (1.08 g, 2.25 mmol)) and $GaMe_3$ (0.520 g, 4.53 mmol) in 30 mL of pentane was allowed to stir for 16 h at room temperature, the pentane was removed at 0 °C to leave a yellow-orange viscous liquid and a small amount of a colorless solid. The pentane that had been removed was observed to "smoke" upon exposure to air due to the presence of $GaMe_3$ formed by a ligand redistribution reaction of the proposed product. Vacuum distillation of the yellow-orange viscous liquid at room temperature for 3 h through a 90° elbow connected to a Schlenk flask that had been cooled to −196 °C produced a colorless liquid (0.307 g) and a small amount of a colorless goo in the neck of the Schlenk flask. A golden-brown liquid (0.619 g) remained in the original distillation flask. Colorless liquid (mostly $Me_2Ga(C_5H_4SiMe_3)$): soluble in pentane and benzene; ^1H NMR (C_6D_6, δ) 6.47 (s br, 1.1, ring-*H*), 6.35 (s br, 1.2, ring-*H*), 6.16 (s br, 0.1, C_5H_5), 0.18 (s, 9.0, $SiMe_3$), 0.12 (s, 0.1, $SiMe_3$), −0.04 (s, 0.4, $SiMe_3$), −0.13 (s, 0.2, $SiMe_3$), −0.38 (s br, 1.9, $GaMe_2$), −0.95 (s br, 1.0, Ga*Me*). Colorless goo in neck of flask (mixture of $Me_2Ga(C_5H_4SiMe_3)$ with impurity of $Me_2Ga(C_5H_5)$): ^1H NMR (C_6D_6, δ) 6.53 (s br, 1.3, ring-*H*), 6.43 (s br, 1.5, ring-*H*), 6.19 (s br, 3.4, C_5H_5), 0.19 (s, 9.0, $SiMe_3$), −0.03 (s, 0.9, $SiMe_3$), −0.13 (s, 0.7, $SiMe_3$), −0.44 (s br, 2.7, $GaMe_2$), −1.03 (s br, 1.4, Ga*Me*). Golden-brown liquid (mixture of $MeGa(C_5H_4SiMe_3)_2$ and $Ga(C_5H_4SiMe_3)_3$): soluble in pentane and benzene; ^1H NMR (C_6D_6) 6.44 (s br, 2.1, ring-*H*), 6.32 (s br, 2.1, ring-*H*), 6.15 (s br, 0.2, C_5H_5), 0.18 (s, 9.0, $SiMe_3$), −0.04 (s, 0.3, $SiMe_3$), −0.12 (s, 0.4, $SiMe_3$), −0.38 (s br, 0.7, $GaMe_2$), −0.94 (s br, 1.4, Ga*Me*).

Attempted Synthesis of $MeGa(C_5H_4SiMe_3)_2$ by Ligand Redistribution Reaction. The reagents $GaMe_3$ (0.0764 g, 0.665 mmol) and $Ga(C_5H_4SiMe_3)_3$ (0.640 g, 1.33 mmol) were combined in 15 mL of pentane at room temperature for 2 h. Then the material volatile at room temperature was removed by vacuum distillation to leave a golden-brown liquid (0.612 g, 85.4% by mass of starting materials). Golden-brown liquid: ^1H NMR (C_6D_6, δ) 6.40 (s br, 1.9, ring-*H*), 6.30 (s br, 3.4, ring-*H*), 6.09 (s br, 0.4, C_5H_5), 0.23 (s, 2.0, $SiMe_3$, $Ga(C_5H_4SiMe_3)_3$), 0.17 (s, 18, $SiMe_3$, $MeGa(C_5H_4SiMe_3)_2$), −0.12 (s, 0.1, vinyl $SiMe_3$), −0.94 (s br, 3.0, Ga*Me*, $MeGa(C_5H_4SiMe_3)_2$).

^1H NMR Spectral Studies of $GaMe_3$ and $Ga(C_5H_4SiMe_3)_3$ in Various Molar Ratios. A small reaction vessel connected to an NMR tube was charged with $Ga(C_5H_4SiMe_3)_3$, and then C_6D_6 followed by the appropriate stoichiometric amount of $GaMe_3$ was added by vacuum distillation. The resulting solution was stirred and poured into the NMR tube, and then the NMR tube was flame sealed. (a) Reagents in 2:1 mol ratio: 0.125 g (0.259 mmol) of $Ga(C_5H_4SiMe_3)_3$ and 0.0592 g (0.516 mmol) of $GaMe_3$; ^1H NMR (C_6D_6, δ) 6.51 (s, 1.2, ring-*H*), 6.43 (s br, 1.1, ring-*H*), 6.19 (s, 0.2, C_5H_5), 0.22 (s, 0.4, $SiMe_3$), 0.18 (s, 9.0, $SiMe_3$), −0.12 (s, 0.5, $SiMe_3$), −0.32 (s br, 7.4, $GaMe_2/GaMe_3$), −0.93 (br, 0.03 Ga*Me*). (b) Reagents in 1:2 mol ratio: 0.0668 g (0.139 mmol) of $Ga(C_5H_4SiMe_3)_3$ and 0.0079 g (0.069 mmol) of $GaMe_3$of $GaMe_3$; ^1H NMR (C_6D_6, δ) 6.45 (s, 2.5, ring-*H*), 6.33 (s, 2.5, ring-*H*), 6.15 (s, 0.4, C_5H_5), 0.17 (s, 18, $SiMe_3$), −0.13 (s, 0.6, $SiMe_3$), −0.28 (s br, 0.5, $Me_2Ga(C_5H_4SiMe_3)$, −0.94 (s br, 3.0, Ga*Me*, $MeGa(C_5H_4SiMe_3)_2$). (c) Reagents in 1:1 mol ratio: 0.265 g (0.550 mmol) of $Ga(C_5H_4SiMe_3)_3$ and 0.0636 g (0.554 mmol) of $GaMe_3$; ^1H NMR (C_6D_6, δ) 6.47 (s br, 2.1, ring-*H*), 6.35 (s br, 1.6, ring-*H*), 6.17 (br, 0.4, C_5H_5), 0.17 (s, 13.5, $SiMe_3$), −0.34 (s br, 3.7, $GaMe_2$, $Me_2Ga(C_5H_4SiMe_3)$, −0.96 (s br, 1.3, $MeGa(C_5H_4SiMe_3)_2$).

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Supporting Information Available: Additional ^1H and ^{13}C NMR spectral data as well as infrared spectral data for the pure compounds are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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