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Synthesis and Characterization of Monomeric Organogallium−Nitrogen Compounds, $Et_2GaNMe[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$, $Me_2GaNMe[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$, $MeGa\{NH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]\}_2$, and $Ga\{NH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]\}_3$

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Four gallium−nitrogen compounds, $Et_2GaNMe[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$, $Me_2GaNMe[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$, $MeGa\{NH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]\}_2$, and $Ga[N(H)C_6H_2(t\text{-}2,4,6\text{-}Bu)_3]_3$, have been prepared by metathetical reactions. The monomeric derivatives $Et_2GaNMe[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$ and $Me_2GaNMe[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$ are of interest because their ^1H NMR spectra at room temperature had resonances indicative of two magnetically nonequivalent organic groups bonded to gallium, a spectral feature consistent with restricted rotation about the gallium−nitrogen bond. Variable-temperature ^1H NMR spectral studies of a toluene solution of $Me_2GaNMe[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$ identified the barrier to rotation about the gallium−nitrogen bond as approximately 71 kJ/mol. This result suggests that steric effects might be responsible. The monomeric compound $MeGa\{NH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]\}_2$ was prepared from $MeGaCl_2$ and $LiNH[C_6H_2(t\text{-}Bu)_3]$ but was also the gallium−nitrogen product when Me_2GaCl was reacted with the same lithium amide in diethyl ether. Experimental data demonstrated that $Me_2GaNH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]$ underwent a ligand redistribution reaction at room temperature to form an equilibrium mixture with $MeGa\{NH[C_6H_2(2,4,6\text{-}t\text{-}Bu)_3]\}_2$ and $GaMe_3$. In contrast, the tertiary amide $Ga\{NH[C_6H_2(t\text{-}Bu)_3]\}_3$ does not readily undergo ligand redistribution reactions with $GaMe_3$.

Introduction

Monomeric compounds with the simplest formula $R_2GaNR^1R^2$ such as $(t\text{-}Bu)_2GaN(t\text{-}Bu)(SiPh_3)$,[1] $(t\text{-}Bu)_2GaN(1\text{-}adamantyl)(SiPh_3)$,[1] $[(2,4,6\text{-}i\text{-}Pr)_3C_6H_2]_2GaNH[(2,6\text{-}i\text{-}Pr)_2C_6H_3]_2$,[1] $[(2,4,6\text{-}t\text{-}Bu)_3C_6H_2]_2GaN(H)Ph$,[2] $R_2GaN(t\text{-}Bu)(BMe_2)$[3] ($R = Me$, Et and CH_2CPhMe_2), and $Et_2GaN(t\text{-}Bu)(BMes_2)$[4] have the potential to exhibit p−p π-bonding[3] between gallium and nitrogen, but the experimental data suggest that these interactions are not significant for determining either their structural features or their unique NMR spectral properties at room temperature. Thus, the GaR_2 and the NR^1R^2 moieties are not coplanar even though each moiety is planar within a given molecule according to the X-ray structural data. Similarly, the asymmetries of the NR^1R^2 moieties have the potential to magnetically distinguish the two organic substituents bonded to gallium, but the substituents were equivalent according to NMR spectra at room temperature. Thus, rotation about the gallium−nitrogen bond in these molecules is not restricted under these conditions. In this paper the preparation and characterization of four new monomeric gallium−nitrogen compounds that incorporate a supermesityl group on nitrogen, $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$, $Me_2GaNMe[C_6H_2(t\text{-}Bu)_3]$, $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$, and $Ga[N(H)C_6H_2(t\text{-}Bu)_3]_3$, are described. The first two are of special interest because of their potential to exhibit magnetically nonequivalent organic groups on gallium if there is restricted rotation about the gallium−nitrogen bond.

Results and Discussion

The new compound $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$, which is closely related to the previously reported derivative $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$,[5] was synthesized in 90% yield by a metathetical reaction between Et_2GaCl[6,7] and $LiNMe[C_6H_2(t\text{-}Bu)_3]$ in pentane and then fully characterized. Even though both gallium−nitrogen compounds are liquids at room temperature and are monomeric according to cryoscopic molecular weight studies in benzene solution in the concentration range of 0.04−0.08 *m*, they have very different chemical properties and ^1H NMR spectra. The new derivative $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$

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was stable to decomposition at temperatures up to 120−130 °C. In contrast, $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ decomposed at room temperature and formed the metallacyclic compound $\{Et\overline{GaNH[C_6H_2(t\text{-}Bu)_2(CMe_2C}H_2)]\}_2$, $GaEt_3$, and $H_2N[C_6H_2(t\text{-}Bu)_3]$.[5] The ^1H NMR spectra of these two gallium−nitrogen monomers are also very different. The spectrum of $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ is consistent with restricted rotation of the $GaEt_2$ group about the gallium−nitrogen bond at 20.7 °C, whereas the two ethyl groups of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ are magnetically equivalent under the same conditions. Thus, a benzene solution of $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ exhibited two sets of sharp resonances of equal intensities for the methyl and methylene protons for the ethyl groups bonded to gallium, whereas $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ had only one set of ethyl gallium resonances. Single resonances for the *N*-methyl, the *ortho* and *para tert*-butyl groups, and the phenyl protons completed the spectrum of $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$. Thus, a methyl group and a supermesityl group on nitrogen are able to restrict rotation about the gallium−nitrogen bond at 20.7 °C and make the ethyl groups on gallium magnetically nonequivalent. Variable-temperature NMR studies of $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ in toluene-d_8 revealed that 75 °C, the highest temperature investigated, did not supply sufficient energy to enable the $GaEt_2$ group to rotate freely and make the ethyl(gallium) protons equivalent.

The synthesis of $Me_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ was undertaken in order to determine if there was restricted rotation of the $GaMe_2$ moiety as there was for the $GaEt_2$ moiety in $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ and, if so, attempt to determine whether steric hindrance between substituents, p−p π-bonding between gallium and nitrogen, or some other factor(s) was responsible. A metathetical reaction between Me_2GaCl[7,8] and $LiNMe[C_6H_2(t\text{-}Bu)_3]$ in pentane provided the desired gallium−nitrogen product $Me_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ as a crystalline solid at room temperature. The compound was readily purified by vacuum sublimation at 60−70 °C and existed as a monomeric species in benzene solution according to cryoscopic molecular weight studies in the concentration range of 0.04−0.08 *m*. The ^1H NMR spectrum of $Me_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ in benzene and toluene indicated restricted rotation of the $GaMe_2$ moiety, as two $Ga-CH_3$ singlets of equal intensity, each with a width at half-height of 8.28 Hz, were observed at 20.7 °C. All other lines in the spectrum were sharp, an observation consistent with free rotation of the $C_6H_2(t\text{-}Bu)_3$ group.

A variable-temperature ^1H NMR spectral study of $Me_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ in d_8-toluene was undertaken in order to learn more about the origin of the restricted rotation about the gallium−nitrogen bond. When the temperature was increased from 20.7 to 30.0 °C, the two lines for the $Ga-CH_3$ groups broadened from 8.28 to 16.08 Hz, whereas all other lines in the spectrum remained sharp. Heating to 40 °C caused more broadening as the width at half-height of each of the Ga-Me lines increased to 37.70 Hz. Coalescence occurred at 51 °C. A further increase in temperature to 60 °C led to sharpening of the single line as the width at half-height decreased to 49.59 Hz. The maximum separation of the two gallium-methyl lines of 0.231 ppm at 20.7 °C, a coalesence temperature of 51 °C, and the approximate formula[9] afforded a calculated barrier to rotation about the gallium−nitrogen bond of 71 kJ/mol. This small barrier is most likely the result of steric interactions between the methyl groups bonded to gallium and the nitrogen substituents, the bulky supermesityl group, and the methyl group. In contrast, when the methyl group on nitrogen was replaced by a proton, as in $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$[5] and $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$ (see below), the steric effects were sufficiently small that free rotation about the gallium−nitrogen bond was observed at 20.7 °C. Thus, all observations suggest that π-bonding between gallium and nitrogen appears to be minimal, if it occurs at all.[1−4] An X-ray structural study of $Me_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ was attempted, but X-ray quality crystals could not be isolated. Single crystals were grown by vacuum sublimation in a sealed tube. However, when the crystals were separated from the wall of the tube in the drybox, they became opaque and did not diffract a beam of X-rays. Recrystallization from pentane was also investigated as a method of crystal growth, but X-ray quality crystals could not be obtained by this method either.

The preparation of $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$ by a metathetical reaction between Me_2GaCl[7,8] and $LiNH[C_6H_2(t\text{-}Bu)_3]$[5] (eq 1) was attempted so that its chemical, physical, and spectral properties could be compared with those of $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$[5] and $Me_2GaNMe[C_6H_2(t\text{-}Bu)_3]$. However, $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$ could not be isolated as a pure compound because it underwent a ligand redistribution reaction to form an equilibrium mixture with $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ and $GaMe_3$ (eq 2) in diethyl ether and pentane, the reaction solvents.

$$Me_2GaCl + LiNH[C_6H_2(t\text{-}Bu)_3] \rightarrow Me_2GaNH[C_6H_2(t\text{-}Bu)_3] + LiCl \quad (1)$$

$$2Me_2GaNH[C_6H_2(t\text{-}Bu)_3] \rightleftharpoons MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2 + GaMe_3 \quad (2)$$

When the synthetic reaction (eq 1) was carried out in diethyl ether, the isolated gallium−nitrogen product was $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$, not $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$. The ^1H NMR spectrum of this product was identical to the compound independently prepared from $MeGaCl_2$ and $LiNH[C_6H_2(t\text{-}Bu)_3]$[5] (see below). The other product, trimethylgallium diethyl ether adduct, must have been removed with the ether during vacuum distillation, a conclusion consistent with its physical properties. When pentane was the reaction solvent, the isolated product was a mixture of $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$ and $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$, two species in the above ligand redistribution equilibrium (eq 2). The remaining species in the above equilibrium, $GaMe_3$, had been removed from the nonvolatile product during vacuum distillation of the solvent, as the flask containing the solvent that was separated by vacuum distillation smoked and smelled of $GaMe_3$ when it was removed from the vacuum line and exposed to air. The ^1H NMR spectrum of the nonvolatile mixture in C_6D_6 confirmed the existence of the equilibrium, as the spectrum exhibited lines for all three methyl gallium compounds

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in eq 2, $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$, $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$, and $GaMe_3$. The presence of both $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$ and $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ permitted the formation of $GaMe_3$ as required by the above equation. The experimental observations for the reactions in diethyl ether and pentane are reconciled if $Me_3Ga{\cdot}OEt_2$ undergoes a ligand redistribution with $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ slower than does $GaMe_3$. Four-coordinate gallium compounds typically undergo ligand redistribution reactions slower than do three-coordinate species. Thus, $Me_3Ga{\cdot}OEt_2$ was removed by vacuum distillation before it could react with $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ and re-form $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$. It is noteworthy that the ^1H NMR resonances assigned to $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$ as part of the equilibrium mixture included only one line for the Ga-Me protons. Thus, neither $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$ nor $Et_2GaNH[C_6H_2(t\text{-}Bu)_3]$ exhibits restricted rotation about the gallium−nitrogen bond at 20.7 °C.

The identity of $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ and its formation by the decomposition of $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$ by a ligand redistribution reaction were confirmed by its independent synthesis and characterization. This compound was prepared in 70% yield by a metathetical reaction between $MeGaCl_2$[10] and $LiNH[C_6H_2(t\text{-}Bu)_3]$[5] in a 1:2 mol ratio in diethyl ether and then purified by recrystallization from ether. This gallium−nitrogen product was a crystalline solid, mp 214.7−216.1 °C, and was monomeric in benzene solution in the concentration range of 0.07−0.03 *m* according to a cryoscopic molecular weight study. The resonances in the ^1H NMR spectrum of pure $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ in benzene were identical to those assigned to this compound, as found in the products of the reaction between Me_2GaCl and $LiNH[C_6H_2(t\text{-}Bu)_3]$ in diethyl ether or pentane (eqs 1 and 2).

The derivative with three bulky substituents, $Ga\{NH[C_6H_2(t\text{-}Bu)_3]\}_3$, was prepared by reacting $GaCl_3$ with excess $LiNH[C_6H_2(t\text{-}Bu)_3]$.[5] This gallium−nitrogen product was soluble in pentane and benzene even though it decomposed at the unusually high temperature of 258−260 °C. When $Ga\{NH[C_6H_2(t\text{-}Bu)_3]\}_3$ was combined with $GaMe_3$ in 1:2 and 2:1 mol ratios in benzene solution in attempts to prepare $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$ and $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ by stoichiometric ligand redistribution reactions, minimal, if any, reaction occurred even after 12 months according to the ^1H NMR spectra of the reaction mixtures. Thus, three $NH[C_6H_2(\textit{t}\text{-}Bu)_3]$ groups are sufficiently bulky to protect the gallium from reaction with $GaMe_3$.

Experimental Section

All compounds were manipulated in a standard vacuum line or in a purified argon atmosphere. The starting materials $GaMe_3$, $GaEt_3$, and Li(n-Bu) were purchased from Strem Chemicals, Inc. and Aldrich Chemical Co., as appropriate, whereas Et_2GaCl[5] and $LiNH[C_6H_2(t\text{-}Bu)_3]$[5] were prepared by using literature methods. Crude products that incorporated the $NH[C_6H_2(t\text{-}Bu)_3]$ ligand as described in the following paragraphs were observed to have an impurity of the free amine $NH_2[C_6H_2(t\text{-}Bu)_3]$ that varied for the preparation of a given compound from 1 to 15%. Extensive studies attempted to identify the source of the amine and the reason for its variability but without success.[5] The amine was not a product of accidental hydrolysis. The provenance of the amine remains unknown. Since the preparations of Me_2GaCl[7,8] and $MeGaCl_2$[10] by ligand redistribution reactions in pentane solutions have not been reported, they are described below. All solvents were dried by conventional procedures. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Parsippany, NJ. The ^1H NMR spectra were recorded at 400 MHz by using a Varian Unity-Inova 400 spectrometer. Proton chemical shifts are reported in δ (ppm) units and are referenced to $SiMe_4$ at δ 0.00 ppm and benzene at δ 7.15 ppm. All samples for NMR spectra were contained in sealed NMR tubes. Infrared spectra were observed for either neat liquids or Nujol mulls of solids, as appropriate, between KBr plates and were recorded with a Perkin-Elmer 683 spectrometer. Melting points were determined with a Mel-Temp by using flame-sealed capillaries filled with purified argon and are uncorrected. Molecular weights were measured cryoscopically for benzene solutions by using an instrument similar to that described by Shriver and Drezdzon.[11]

Preparation of Me_2GaCl. A 1.15 g (10.0 mmol) sample of $GaMe_3$ was added by vacuum distillation to 0.881 g (5.00 mmol) of freshly sublimed $GaCl_3$ dissolved in approximately 25 mL of pentane. The reaction mixture was warmed from −196 °C to room temperature over a 10 min period and then stirred overnight. Removal of solvent by vacuum distillation at 0 °C produced a colorless solid, which was purified by sublimation at room temperature from the original reaction flask through a glass elbow into a Schlenk flask maintained at −196 °C. The product Me_2GaCl (1.67 g 12.4 mmol) was isolated in 82% yield as a colorless, crystalline solid. Me_2GaCl: mp 45.3−45.5 °C (lit.[7] 45 °C); ^1H NMR (C_6D_6,δ) 0.18 (s, Ga−CH_3).

Preparation of $MeGaCl_2$. A flask charged with 1.15 g of freshly sublimed $GaCl_3$ (6.52 mmol) was attached to a 90° glass elbow which had been connected to a Schlenk flask. Then approximately 20 mL of pentane and 0.375 g of $GaMe_3$ (3.26 mmol) were vacuum distilled into the flask. As the reaction mixture warmed to room temperature over 10 min, a colorless precipitate formed. After the reaction mixture had been stirred for 12 h, the solvent was removed by vacuum distillation at room temperature. The resulting colorless solid was purified at room temperature by dynamic sublimation through the glass elbow into the Schlenk flask maintained at −196 °C. The product $MeGaCl_2$ (1.36 g, 8.74 mmol) was isolated in 89.3% yield. $MeGaCl_2$: mp 78.4−78.9 °C (lit.[10] 75−76 °C); ^1H NMR (THF-d_8, δ) 0.14 (s, Ga−CH_3).

Preparation of $LiNMe[C_6H_2(t\text{-}Bu)_3]$. A pressure-equalizing addition funnel was charged in the drybox with 6.21 g (22.6 mmol) of $HNMe[C_6H_2(t\text{-}Bu)_3]$ and connected to a 500 mL three-necked flask that was equipped with a 24/40 adapter with a Teflon stopcock and a rubber septum. Then a solution of Li(n-Bu) (1.6 M in hexanes, 15 mL, 24 mmol) was added by syringe to the three-necked flask under cover of argon. Finally, approximately 50 mL of pentane was transferred by cannula both to the addition funnel to dissolve the amine and to the flask to dilute the Li(n-Bu). The solution of Li(n-Bu) was cooled to 0 °C, and then the solution of $HNMe[C_6H_2(t\text{-}Bu)_3]$ was added with stirring at a rate of about 20 drops/min. Since no precipitate was observed during the addition of the amine, the reaction mixture was allowed to warm to room temperature overnight, after which time a colorless precipitate had formed. The precipitate was isolated by filtration and washed three times with cold solvent to yield 3.05 g of $LiNMe[C_6H_2(t\text{-}Bu)_3]$ (10.8 mmol, 48.1% based on $HNMe[C_6H_2(t\text{-}Bu)_3]$). $LiNMe[C_6H_2(t\text{-}Bu)_3]$: ^1H NMR (THF-d_8, δ) 7.09 (s, Ar−H, 2H), 3.10 (s, N−CH_3, 3H), 1.48 (s, *o*-Ph−(t-Bu), 18H), 1.23 (s, *p*-Ph−(t-Bu), 9H).

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Preparation of $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$. A solution of 1.08 g (6.60 mmol) of Et_2GaCl in approximately 25 mL of pentane was added to a suspension of 2.01 g (7.12 mmol) of $LiNMe[C_6H_2(t\text{-}Bu)_3]$ in about 25 mL of pentane that had been cooled to 0 °C. The reaction mixture was stirred for 2 h and then filtered. Two additional extractions of the precipitate separated the pentane-soluble product from LiCl and unreacted lithium amide. Removal of the solvent by vacuum distillation provided a mobile liquid that was purified by vacuum distillation by using an oil bath at 120−130 °C. The final product, $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ (2.38 g, 5.91 mmol, 89.5% yield based on Et_2GaCl), was isolated as a colorless mobile liquid that was stable to overnight heating at 65 °C. $Et_2GaNMe[C_6H_2(t\text{-}Bu)_3]$: ^1H NMR (C_6D_6, δ) 7.53 (s, Ph−H, 2H), 3.00 (s, $N-CH_3$, 3H), 1.55 (s, *o*-Ph−(t-Bu), 18H), 1.32 (s, *p*-Ph−(t-Bu), 9H), 1.24 (t, $J_{C-H} = 8$ Hz, $Ga-CH_2CH_3$, 3H), 0.97 (t, $J_{C-H} = 8$ Hz, $Ga-CH_2CH_3$, 3H), 0.75 (q, $J_{C-H} = 8$ Hz, $Ga-CH_2CH_3$, 2H), 0.47 (q, $J_{C-H} = 8$ Hz, $Ga-CH_2CH_3$, 2H). Anal. Calcd for $C_{23}H_{42}GaN$: C, 68.67; H, 10.52. Found: C, 69.40; H, 10.43. Cryoscopic molecular weight, benzene solution, formula weight 402 (observed molality, observed molecular weight, association): 0.079, 393, 0.98; 0.052, 400, 1.00; 0.029, 390, 0.97.

Preparation of $Me_2GaNMe[C_6H_2(t\text{-}Bu)_3]$. A solution of 0.793 g (5.86 mmol) of Me_2GaCl in approximately 25 mL of pentane was added to 1.65 g (5.86 mmol) of $LiNMe[C_6H_2(t\text{-}Bu)_3]$ suspended in 25 mL of pentane at 0 °C and stirred for 2 h. The reaction mixture was filtered to separate LiCl. After the residue was washed two additional times with pentane, the solvent was removed by vacuum distillation and a viscous material remained. Subsequent dynamic evacuation of the crude product for 12 h produced a solid that was purified by vacuum sublimation at 60−70 °C. The compound $Me_2GaNMe[C_6H_2(t\text{-}Bu)_3]$ (1.81 g, 4.83 mmol) was isolated as a colorless solid in 82.4% yield. $Me_2GaN[MeC_6H_2(t\text{-}Bu)_3]$: mp 73.6−74.2 °C; ^1H NMR (C_6D_6, δ) 7.57 (s, Ph−H, 2H), 2.99 (s, $N-CH_3$, 3H), 1.54 (s, *o*-Ph−(t-Bu), 18H), 1.32 (s, *p*-Ph−(t-Bu), 9H), −0.02 (s, $Ga-CH_3$, 3H), −0.21 (s, $Ga-CH_3$, 3H); ($C_6D_5CD_3$, δ) 7.50 (s, Ph−H, 2H), 2.98 (s, $N-CH_3$, 3H), 1.52 (s, *o*-Ph−(t-Bu), 18H), 1.32 (s, *p*-Ph−(t-Bu), 9H), −0.002 (s, $Ga-CH_3$, 3H), −0.228 (s, $Ga-CH_3$, 3H); IR (Nujol, cm^{-1}) 2790 (s), 1598 (m), 1552 (w), 1472 (s), 1430 (s), 1410 (s), 1388 (vs), 1359 (s), 1282 (m), 1260 (s), 1237 (s), 1210 (s), 1199 (s), 1170 (m, br), 1142 (m), 1118 (s), 1050 (s), 930 (w), 838 (s), 816 (w), 788 (m), 765 (s), 745 (s), 719 (s), 643 (m), 589 (s), 540 (m), 518 (w), 460 (w), 419 (w). Anal. Calcd for $C_{21}H_{38}GaN$: C, 67.40; H, 10.23. Found: C, 67.84; H, 10.71. Cryoscopic molecular weight, benzene solution, formula weight 374 (observed molality, observed molecular weight, association): 0.077, 374, 1.00; 0.059, 373, 1.00; 0.040, 375, 1.00. Crystals were grown by placing a sample of the compound in a sealed evacuated tube above the vent of an oven maintained at 150 °C. However, when the crystals were removed from the wall of the tube in the drybox, they became opaque and did not diffract a beam of X-rays. Attempts to grow X-ray quality crystals by recrystallization from a pentane solution were unsuccessful.

Reaction of Me_2GaCl and $LiNH[C_6H_2(t\text{-}Bu)_3]$ in Diethyl Ether. The reagents 0.431 g (3.19 mmol) of Me_2GaCl and 0.908 g (3.39 mmol) of $LiNH[C_6H_2(t\text{-}Bu)_3]$ were combined in diethyl ether at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The reaction mixture was filtered, and then the insoluble components were washed two times with the reaction solvent. The components that were volatile at room temperature were removed from the soluble fraction by vacuum distillation, and 0.973 g of a colorless solid was obtained. This crude product was identified by ^1H NMR spectroscopy as primarily $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ with an impurity of $H_2N[C_6H_2(t\text{-}Bu)_3]$:[5] mp 175.6−182.6 °C; ^1H NMR (C_6D_6, δ) 7.55 (s, Ph-H, $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$), 7.40 (s, Ph−H, $H_2N[C_6H_2(t\text{-}Bu)_3]$), 3.63 (s, N−H, $H_2N[C_6H_2(t\text{-}Bu)_3]$), 3.22 (s, N−H, $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$), 1.63 (s, *o*-Ph−(t-Bu), $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$), 1.40 (s, *o*-Ph−(t-Bu), $H_2N[C_6H_2(t\text{-}Bu)_3]$), 1.39 (s, *p*-Ph−(t-Bu), $H_2N[C_6H_2(t\text{-}Bu)_3]$), 1.35 (s, *p*-Ph−(t-Bu) $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$), −0.31 (s, Me, $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$).

Reaction of Me_2GaCl and $LiNH[C_6H_2(t\text{-}Bu)_3]$ in Pentane. A flask was charged with 0.507 g (3.75 mmol) of Me_2GaCl, while 1.02 g (3.81 mmol) of $LiNH[C_6H_2(t\text{-}Bu)_3]$ was placed in a Schlenk flask connected by means of a medium-porosity glass frit. After approximately 25 mL of pentane had been added to each flask, the suspension of $LiNH[C_6H_2(t\text{-}Bu)_3]$ was cooled to 0 °C. Then the solution of Me_2GaCl was added, and the mixture was stirred for 2 h. After the reaction mixture was filtered, the residue was washed two additional times. Removal of the pentane by vacuum distillation produced 1.195 g of a colorless solid. This crude product was identified by ^1H NMR spectroscopy as a mixture of $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$ and $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ with a small impurity of $H_2N[C_6H_2(t\text{-}Bu)_3]$:[5] mp 110−160 °C; ^1H NMR (C_6D_6, δ) 7.55 (s, Ph−H, $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$), 7.51 (s, Ph−H, $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$), 7.40 (s, Ph−H, $H_2N[C_6H_2(t\text{-}Bu)_3]$), 3.63 (s, N−H, $H_2N[C_6H_2(t\text{-}Bu)_3]$), 3.49 (s, N−H, $Me_2GaNH[C_6H_2\ (t\text{-}Bu)_3]$), 3.22 (s, N−H, $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$), 1.63 (s, *o*-Ph−(t-Bu), $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$), 1.51 (s, *o*-Ph−(t-Bu), $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$), 1.40 (s, *o*-Ph−(t-Bu), $H_2NC_6H_2(t\text{-}Bu)_3$), 1.39 (s, n*p*-Ph−(t-Bu), $H_2N[C_6H_2(t\text{-}Bu)_3]$), 1.36 (s, *p*-Ph−(t-Bu), $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$), 1.35 (s, *p*-Ph−(t-Bu), $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$), −0.15 (s, Me, $Me_2GaNH[C_6H_2(t\text{-}Bu)_3]$), −0.26 (s, Me, $GaMe_3$), −0.31 (s, Me, $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$).

Preparation of $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$. A Solv-seal Schlenk flask with 1.02 g (3.82 mmol) of $LiNH[C_6H_2(t\text{-}Bu)_3]$ was connected by means of a medium-porosity frit to a flask that contained 0.289 g (1.86 mmol) of $MeGaCl_2$. Approximately 25 mL of diethyl ether was vacuum distilled into the apparatus at −196 °C. After the ether was divided between the two flasks, the flask containing the suspension of $LiNH[C_6H_2(t\text{-}Bu)_3]$ in ether was cooled to 0 °C and the solution of $MeGaCl_2$ was added. The resulting mixture was stirred for 12 h and then filtered to remove LiCl and excess $LiNH[C_6H_2(t\text{-}Bu)_3]$. The residue was washed three additional times. The resulting solution was cooled to −30 °C to induce crystallization. Removal of the solvent by vacuum distillation at room temperature produced 0.792 g of $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$ (1.31 mmol, 70.4% yield based on $MeGaCl_2$) as a colorless solid. $MeGa\{NH[C_6H_2(t\text{-}Bu)_3]\}_2$: mp 214.7−216.1 °C; ^1H NMR (C_6D_6, δ) 7.55 (s, Ph−H, 4H), 3.23 (s, N−H, 2H), 1.63 (s, *o*-Ph−(t-Bu), 36H), 1.35 (s, *p*-Ph−(t-Bu), 18H), −0.30 (s, $GaCH_3$, 3H); IR (Nujol, cm^{-1}) 3420 (m), 1599 (w), 1423 (s), 1360 (vs), 1262 (m), 1242 (m), 1220 (m), 1193 (m), 1111 (m), 1018 (w), 930 (w), 918 (w), 865 (m), 829 (m), 813 (w), 785 (w), 745 (w), 720 (w), 620 (w, br), 470 (w), 430 (w, br). Anal. Calcd for $C_{37}H_{63}GaN_2$: C, 73.38; H, 10.49; N, 4.63. Found: C, 73.78; H, 10.80; N, 4.31. Cryoscopic molecular weight, benzene solution, formula weight 606 (observed molality, observed molecular weight, association): 0.068, 627, 1.03; 0.054, 616, 1.02; 0.033, 612, 1.01.

Preparation of $Ga\{NH[C_6H_2(t\text{-}Bu)_3]\}_3$. A Schlenk flask charged with 0.148 g (0.840 mmol) of freshly sublimed $GaCl_3$ was connected by means of a medium frit to a second flask charged with 0.718 g (2.69 mmol) of $LiNH[C_6H_2(t\text{-}Bu)_3]$. Then, approximately 35 mL of benzene was added by vacuum distillation to each flask. After the flask containing the $LiNH[C_6H_2(t\text{-}Bu)_3]$ was cooled with ice, the $GaCl_3$ solution was added over a 2 h period to the slurry of $LiNH[C_6H_2(t\text{-}Bu)_3]$. The reaction mixture was permitted to warm to room temperature and was stirred overnight. The benzene was removed by vacuum distillation and approximately 70 mL of pentane was added. The product mixture was filtered and then washed four additional times to separate the LiCl and excess $LiNH[C_6H_2(t\text{-}Bu)_3]$ from the soluble product. Recrystallization of the product from pentane at −78 °C yielded 0.475 g of $Ga\{NH[C_6H_2(t\text{-}Bu)_3]\}_3$ (0.558 mmol, 66.5% yield based on $GaCl_3$) as a colorless solid: mp 258−260 °C (dec); ^1H NMR (C_6D_6, δ) 7.35

(s, Ph−H, 6H), 3.84 (s, N−H, 3H), 1.41 (s, *o*-Ph−(*t*-Bu), 54H), 1.36 (s, *p*-Ph−(*t*-Bu), 27H); IR (Nujol, cm^{-1}): 3400 (vw, br), 1580 (vw), 1359 (vs), 1330 (m), 1280 (m), 1237 (m), 1220 (s), 1195 (m), 1162 (w), 1108 (m), 870 (m), 828 (m), 809 (vw), 780 (w). Anal. Calcd for $C_{54}H_{90}GaN_3$: C, 76.21; H, 10.66. Found: C, 75.85; H, 11.29.

Ligand Redistribution Reactions between Ga{NH[C_6H_2(t-Bu)$_3$]}$_3$ and GaMe$_3$ in 2:1 and 1:2 Mol Ratios. (a) 2:1 Mol Ratio. An NMR tube was charged with 0.172 g (0.202 mmol) of Ga{NH[C_6H_2(t-Bu)$_3$]}$_3$ and 0.0116 g (0.101 mmol) of GaMe$_3$. Then ∼0.6 mL of C_6D_6 was added by vacuum distillation, and the tube was flame sealed. ^{1}H NMR (C_6D_6, δ, 12 months): 7.35 (s, Ph−H), 3.83 (s, N−H), 1.40 (s, *o*-Ph−(*t*-Bu)), 1.36 (s, *p*-Ph−(*t*-Bu), 27H), −0.15 (s, GaCH$_3$).

(b) 1:2 Mol Ratio. The reagents, 0.0567 g (0.0666 mmol) of Ga{NH[C_6H_2(t-Bu)$_3$]}$_3$, 0.0153 g (0.133 mmol) of GaMe$_3$, and ∼0.6 mL of C_6D_6, were combined in an NMR tube, and then the ^{1}H NMR spectra were recorded. ^{1}H NMR (C_6D_6, δ, 12 months): 7.35 (s, Ph−H), 3.83 (s, N−H), 1.40 (s, *o*-Ph−(*t*-Bu)), 1.36 (s, *p*-Ph−(*t*-Bu), 27H), −0.15 (s, GaCH$_3$).

Variable-Temperature ^{1}H NMR Spectra of Me$_2$GaNMe[C_6H_2(t-Bu)$_3$]. The temperature dependence of the spectrum was investigated in toluene-*d*$_8$. Increasing the temperature from 20.7 to 60 °C resulted in broadening of the two Ga-Me lines of equal intensity until coalesence was observed at 51 °C. Then, the line sharpened at 60 °C, the highest temperature studied. All other lines in the spectrum were unchanged over this temperature range. The measurements of the widths of the Ga-Me lines at half-height were determined by using the Varian VXR-400 program. The approximate formula[9] with the coalesence temperature of 51 °C and the maximum peak separation of 0.231 ppm afforded a rotation barrier around the gallium−nitrogen bond of 71.5 kJ/mol.

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