Syntheses, Structure, and Reactivity of 2,6-Dimesitylphenyl-Based Sterically Demanding Gallium Aryls

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Reaction of gallium chloride with (2,6-dimesitylphenyl)lithium, $(Mes_2C_6H_3)Li$ (Mes = 2,4,6-$Me_3C_6H_2$), gives bis[(dimesitylphenyl)gallium dichloride], $[(Mes_2C_6H_3)GaCl_2]_2$, **I**. Treatment of **I** with {2-[(dimethylamino)methyl]phenyl}lithium, $[2\text{-}(Me_2NCH_2)C_6H_4]Li$, affords (dimesitylphenyl)-2-((dimethylamino)methyl)phenylgallium chloride, $(Mes_2C_6H_3)[2\text{-}(Me_2NCH_2)\text{-}C_6H_4]GaCl$, **II**. Reaction of $(Mes_2C_6H_3)Li$ with gallium bromide affords bis(dimesitylphenyl)-gallium bromide, $(Mes_2C_6H_3)_2GaBr$, **III**, while reaction of **I** with (Mes)Li yields (dimesitylphenyl)dimesitylgallium, $(Mes_2C_6H_3)(Mes)_2Ga$, **IV**. Gallium aryls **I**−**IV** have been characterized by elemental analyses, ^1H and ^{13}C NMR and IR spectroscopies, and single-crystal X-ray diffraction. **I** assumes a μ^2-chloro-bridged dimeric structure, while the coordination of gallium in **II** is completed by one $Mes_2C_6H_3$ ligand and one chloride ligand and is intramolecularly stabilized by the nitrogen atom of $[2\text{-}(Me_2NCH_2)C_6H_4]$. **III** assumes a rare T-shaped coordination about the gallium center (C−Ga−C 153.5(2)°), while **IV** represents, arguably, the most sterically crowded trigonal planar gallium aryl reported with the aromatic rings about the GaC_3 plane approaching 90°.

Introduction

Sterically demanding substituted aryl ligands have assumed a prominent role in group 13 organometallic chemistry. That the structure and properties of a given compound may be dramatically tuned as a function of ligand steric loading has proven to be a fruitful means to a wide variety of interesting organometallic substances with intriguing properties. This practice has assumed particular significance in the organometallic chemistry of gallium. The 2,6-dimesitylphenyl ligand, $Mes_2C_6H_3$ (Mes = 2,4,6-$Me_3C_6H_2$), is quite significant in this regard. Herein, we report the syntheses, molecular structure, and reactivity of a number of 2,6-dimesitylphenyl-based sterically demanding gallium aryls. The dimeric bis[(dimesitylphenyl)gallium dichloride], $[(Mes_2C_6H_3)GaCl_2]_2$, **I**, and an intramolecularly stabilized organogallium compound in (dimesitylphenyl)-2-((dimethylamino)methyl)phenylgallium chloride, $(Mes_2C_6H_3)[2\text{-}(Me_2NCH_2)C_6H_4]GaCl$, **II**, are reported. The dimeric bis(arylgallium dichloride) was obtained from reaction of gallium chloride with (dimesitylphenyl)-lithium, while the mono-chloride, **II**, was isolated from reaction of **I** with {2-[(dimethylamino)methyl]phenyl}-lithium, $[2\text{-}(Me_2NCH_2)C_6H_4]Li$. Bis(dimesitylphenyl)-gallium bromide, $(Mes_2C_6H_3)_2GaBr$, **III**, isolated from reaction of gallium bromide with (2,6-dimesitylphenyl)-lithium, assumes a rare T-shaped coordination about the metal center, while (dimesitylphenyl)dimesitylgallium, $(Mes_2C_6H_3)(Mes)_2Ga$, **IV**, was isolated from reaction of **I** with (Mes)Li. **IV** represents a most sterically crowded trigonal planar gallium aryl, with the coordination sphere of the metal center being saturated by one dimesitylphenyl ligand and two mesityl ligands. The four sterically demanding gallium aryls discussed herein are testimony to the concept of ligand steric loading and the corresponding extremes which may be approached.

Experimental Section

General Comments. Standard Schlenk techniques were employed in conjunction with an inert atmosphere drybox (M Braun Labmaster 130). Solvents were distilled with sodium benzophenone under an atmosphere of nitrogen prior to use. Nitrogen was passed through copper-based purification and molecular sieves drying columns prior to use. Gallium bromide, gallium chloride, *N*,*N*-((dimethylamino)methyl)benzene, and 2-bromomesitylene were purchased from Aldrich Chemical Co. (Milwaukee, WI), while 2,6-dibromoaniline was purchased from Lancaster Synthesis Inc. (Windham, NH). Both 2,6-dimesityl-1-iodobenzene, $(Mes_2C_6H_3)I$,[1] and [2-((dimethylamino)methyl)phenyl]lithium, $[2\text{-}(Me_2NCH_2)C_6H_4]Li$,[2] were prepared as previously noted. Elemental analyses were performed by E + R Microanalytical Laboratories (Corona, NY). IR spectra were recorded on a Perkin-Elmer 1500 spectrometer, while NMR spectra were recorded on a Bruker AC-300 spectrometer. X-ray intensity data were collected on a Siemens *P4* diffractometer (50kV/40mA). Chemical shifts are reported in parts per million.

Synthesis of $[(Mes_2C_6H_3)GaCl_2]_2$, I. A solution of $(Mes_2C_6H_3)Li$ (0.80 g, 2.5 mmol) in diethyl ether (40 mL) was added over a period of 10 min to a diethyl ether (30 mL) solution of $GaCl_3$ (0.41 g, 2.5 mmol) at −78 °C. The reaction mixture was stirred for 3 h and allowed to warm to room temperature over a period of 2 h. A yellow solution resulted, along with a precipitate (LiCl). The mixture was stirred for an additional 30 h and filtered. The volatiles were completely removed in vacuo (60 °C/0.01 mmHg). The yellow viscose residue was extracted with hexane (150 mL). Cooling the yellow solution to −25 °C for 10 h resulted in an oil residue and some colorless crystals. The colorless solution was separated from the oil residue and crystalline residue (presumably $GaCl_3\cdot(Et_2O)_n$) by

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Table 1. Crystallographic Data

	I, $[(Mes_2C_6H_3)GaCl_2]_2$	**II**, $(Mes_2C_6H_3)$-$[2\text{-}(Me_2NCH_2)C_6H_4]GaCl$	**III**, $(Mes_2$-$C_6H_3)_2GaBr$	**IV**, $(Mes_2$-$C_6H_3)(Mes)_2Ga$
empirical formula	$C_{48}H_{50}Cl_4Ga_2$	$C_{33}H_{37}ClGaN$	$C_{48}H_{50}GaBr$	$C_{42}H_{47}Ga$
fw	908.12	552.80	776.51	621.52
color habit	colorless, cubic	colorless, cubic	colorless, cubic	colorless, cubic
space group	orthorhombic, *Pcba* (No. 61)	triclinic, $P\bar{1}$ (No. 2)	monoclinic, $P2_1/c$ (No. 14)	monoclinic, *C*2/*c* (No. 15)
unit cell dimens				
a (Å)	18.232(7)	8.154(3)	12.205(4)	22.942(7)
b (Å)	20.992(8)	18.446(7)	20.653(6)	10.057(4)
c (Å)	24.203(7)	20.566(7)	16.413(8)	16.855(7)
α (deg)		73.48(1)		
β (deg)		81.35(2)	100.59(3)	115.35
γ (deg)		88.32(2)		
formula units/cell	8	4	4	4
vol (Å^3)	9263(6)	2932(2)	4067(3)	3514(2)
D_{calc} (g/cm^3)	1.302	1.253	1.268	1.175
no. of unit cell reflns	30	25	25	25
maximum 2*θ* angle	40°	45°	45°	45°
no. of reflns, unique	4311	7492	5548	2274
no. of reflns, obsd [$I > 2\sigma(I)$]	2391	5418	3851	1668
no. of params refined	482	649	451	196
abs coeff (mm^{-1})	1.425	1.051	1.690	0.809
refinement method	least-squares on F^2	least-squares on F^2	least-squares on F^2	least-squares on F^2
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.076; wR2 = 0.202	R1 = 0.044; wR2 = 0.108	R1 = 0.053; wR2 = 0.145	R1 = 0.053; wR2 = 0.144
R indices (all data)	R1 = 0.156; wR2 = 0.256	R1 = 0.074; wR2 = 0.134	R1 = 0.083; wR2 = 0.169	R1 = 0.079; wR2 = 0.179
goodness of fit	*S* = 1.071	*S* = 0.998	*S* = 1.011	*S* = 1.035
largest diff. peak (e$^-$/Å^3)	0.972	0.375	0.428	0.413

filtration, during which the temperature was constantly kept at −78 °C. This process was repeated twice. The colorless filtrate was then reduced to ca. 60 mL and stored at −25 °C. Large cubic colorless crystals of **I** formed after a couple of days. Reducing the volume of the rest solution to about 30 mL afforded more crystalline compound **I** (0.75 g, 0.83 mmol). Yield: 66%. Mp 218−219 °C. Anal. Calcd (found) for $C_{48}H_{50}Ga_2Cl_4$: C, 63.48 (63.94); H, 5.55 (6.36). ^{1}H NMR (300 MHz, 298 K, THF-d_8): 2.01 (s, 12H, *o*′-C$\boldsymbol{H}_3$), 2.27 (s, 6H, *p*′-C$\boldsymbol{H}_3$), 6.85 (s, 4H, aromatic protons), 6.89−6.95 (m, 3H, aromatic protons). ^{13}C NMR (300 MHz, 298 K, THF-d_8): 21.3 (*o*′-$\boldsymbol{C}$H$_3$), 21.7 (*p*′-$\boldsymbol{C}$H$_3$), 128.2, 128.8, 129.3, 130.8, 136.6, 137.3, 137.8, 150.6 (aromatic carbon atoms). IR (KBr, Nujol): 1647 (m), 1608 (m), 1548 (m), 1533 (m), 1257 (s), 1150 (m), 1081 (s), 1013 (s), 796 (s), 722 (s), 668 (m), 577 (w).

Synthesis of $(Mes_2C_6H_3)[2\text{-}(Me_2NCH_2)C_6H_4]GaCl$, II. A diethyl ether (50 mL) solution of $[2\text{-}(Me_2NCH_2)C_6H_4]Li$ (0.14 g, 1.0 mmol) was slowly added to a diethyl ether (30 mL) solution of **I** (0.45 g, 0.50 mmol) at −78 °C. The reaction mixture was stirred for 3 h and allowed to warm to room temperature over a period of 2 h, and then stirred for additional 30 h. The mixture was filtered, and the solvent of the resulting yellow solution was removed by vacuum distillation. The residue was extracted with hexane (50 mL). The volume of the solution was reduced *in vacuo*. Cooling the concentrated solution at −25 °C for a week afforded colorless needle crystals of **II** (0.40 g, 0.70 mmol). Yield: 72%. Mp 242 °C. X-ray quality crystals were grown from a 1:1 diethyl ether−hexane mixture. Anal. Calcd. (found) for $C_{33}H_{37}NGaCl$: C, 71.69 (70.98); H, 6.75 (7.67); N, 2.53 (2.51). ^{1}H NMR (300 MHz, 298 K, THF-d_8): 2.07 (s, 12H, *o*′-C$\boldsymbol{H}_3$), 2.11 (s, 6H, *p*′-C$\boldsymbol{H}_3$), 2.18 (s, 2H, N−C$\boldsymbol{H}_2$−), 2.33 (s, 6H, N−C$\boldsymbol{H}_3$), 6.78−6.97 (m, 11H, aromatic protons). ^{13}C NMR (300 MHz, 298 K, THF-d_8): 21.4 (*o*′-$\boldsymbol{C}$H$_3$), 22.3 (*p*′-$\boldsymbol{C}$H$_3$), 44.5 (N−$\boldsymbol{C}$H$_2$−), 45.8 (N−$\boldsymbol{C}$H$_3$), 124.5, 127.3, 128.1, 129.0−129.8 (multiple peaks overlapping), 130.8, 137.4, 138.0, 139.1, 147.2, 147.5, 148.0 (aromatic carbon atoms). IR (KBr, Nujol): 1601 (m), 1563 (w), 1303 (w), 1249 (w), 1173 (w), 1150 (w), 1112 (w), 1073 (m), 1029 (m), 990 (m), 890 (m), 798 (m), 730 (s), 714 (w).

Synthesis of $(Mes_2C_6H_3)_2GaBr$, III. A solution of $(Mes_2C_6H_3)Li$ (3.26 g, 10 mmol) in diethyl ether (30 mL) was added to a solution of $GaBr_3$ (1.55 g, 5 mmol) in diethyl ether (30 mL) at −78 °C. The reaction mixture was stirred for 3 h and then allowed to warm to room temperature. The reaction was stirred for an additional 48 h, after which a yellow solution resulted with a precipitate (LiBr). Upon filtration and subsequent cooling to −25° C for 4 days, colorless X-ray quality crystals were obtained 2.87 g (3.6 mmol). Yield: 74%. Mp 176 °C. Anal. Calcd (found) for $C_{48}H_{50}GaBr$: C, 74.10 (73.44); H, 6.50 (6.60). ^{1}H NMR (300 MHz, 298 K, THF-d_8): 1.67 (s, 24H, *o*′-C$\boldsymbol{H}_3$), 2.31 (s, 12H, *p*′-C$\boldsymbol{H}_3$), 6.62−6.80 (m, 6H, aromatic protons), 6.82 (s, 8H, aromatic protons). ^{13}C NMR (300 MHz, 298 K, THF-d_8): 23.9 (*o*′-CH$_3$), 25.2 (*p*′-$\boldsymbol{C}$H$_3$), 131.1, 131.9, 132.2, 139.5, 140.0, 140.6, 145.0, 150.2 (aromatic carbons).

Synthesis of $(Mes_2C_6H_3)(Mes)_2Ga$, IV. Method A. A solution of $(Mes_2C_6H_3)Li$ (1.65 g, 5 mmol) in diethyl ether (30 mL) was added to a solution of $GaCl_3$ at −78 °C and stirred for 3 h. The reaction mixture was allowed to warm to room temperature and stirred for an additional 48 h. A yellow solution and white precipitate (LiCl) resulted. The resulting solution containing **I** was then filtered into a Schlenk flask previously charged with (Mes)Li (1.27 g, 10 mmol) in diethyl ether solution (40 mL). This solution was stirred at room temperature for 48 h. The solvent was removed, revealing a residue which was extracted with hexane (40 mL). The solution was concentrated to approximately 20 mL and cooled to −25 °C for 8 days, which resulted in colorless X-ray quality crystals.

Method B. To a solution of $GaCl_3$ (0.88 g, 5 mmol) in diethyl ether (30 mL) at −78 °C was added a solution of (Mes)-Li (1.28g, 10 mmol) in diethyl ether solution (30 mL). The reaction mixture was stirred for 3 h and then allowed to warm to room temperature. Following additional stirring for 48 h, the resultant yellow solution was filtered into a Schlenk flask charged with $(Mes_2C_6H_3)Li$ (1.63 g, 5 mmol) in diethyl ether solution. The reaction mixture was stirred for another 30 h and then filtered. The solvent of the yellow solution was removed by vacuum distillation, revealing a residue which was extracted with hexane (40 mL). Concentration to about 20 mL and subsequent cooling for 1 week afforded colorless crystals (1.85 g, 3.0 mmol). Yield: 60%. Mp 180−181 °C. Anal. Calcd (found) for $C_{42}H_{47}Ga$: C, 81.16 (80.40); H, 7.62 (7.43). ^{1}H NMR (300 MHz, 298 K, toluene-d_8): 1.84 (s, 12H, *o*-C$\boldsymbol{H}_3$); 1.94 (s, 12H, *o*′-C$\boldsymbol{H}_3$), 2.09 (s, 6H, p-C$\boldsymbol{H}_3$), 2.13 (s, 6H, *p*′-C$\boldsymbol{H}_3$), 6.54 (s, 4H, aromatic protons), 6.56 (s, 4H, aromatic protons), 6.60−

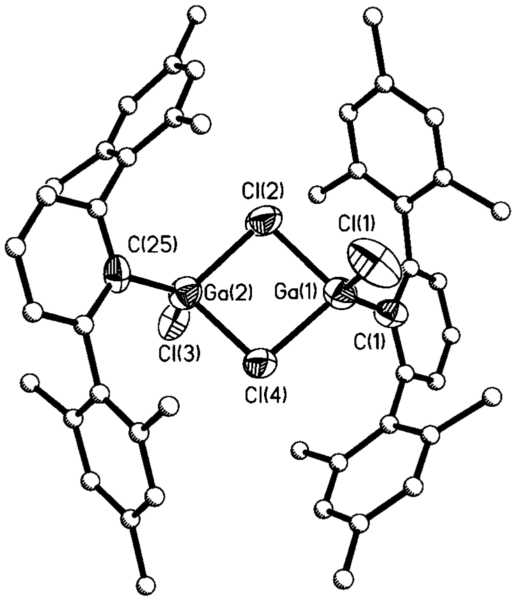

Figure 1. Molecular structure of $[(Mes_2C_6H_3)GaCl_2]_2$, **I**. Selected bond distances (Å) and Angles (deg): Ga(1)−C(1) 1.96(1); Ga(1)−Cl(1) 2.172(5); Ga(1)−Cl(2) 2.333 (5); Ga-(1)−Cl(4) 2.324(4); Ga(2)−C(25) 1.934(1); Ga(2)−Cl(2) 2.323-(5); Ga(2)−Cl(3) 2.290 (4); Ga(2)−Cl(4) 2.320 (4); C(1)−Ga(1)−Cl(1) 126.6(4); C(1)−Ga(1)−Cl(4) 116.2(4); Cl(1)−Ga(1)−Cl(4) 103.0(2); C(1)−Ga(1)−Cl(2) 115.0(4); Cl(1)−Ga(1)−Cl(2) 101.3(2); Cl(4)−Ga(1)−Cl(2) 86.8(2); Ga(2)−Cl(2)−Ga(1) 92.6(2); C(25)−Ga(2)−Cl(3) 126.0(4); C(25)−Ga(2)−Cl(4) 114.8; Cl(3)−Ga(2)−Cl(4) 102.8(2); C(25)−Ga(2)−Cl(2) 115.9(5); Cl(3)−Ga(2)−Cl(2) 102.9(2); Cl(4)−Ga(2)−Cl(2) 87.1(2); Ga(2)−Cl(4)−Ga(1) 92.9(2).

6.94 (m, 3H, aromatic protons). ^{13}C NMR (300 MHz, 298 K, toluene-d_8): 20.98 (o-$\mathbf{C}H_3$), 21.39 (p-$\mathbf{C}H_3$) 24.8 (o'-$\mathbf{C}H_3$), 25.7 (p'-$\mathbf{C}H_3$), 126.8, 127.9, 128.1, 128.3, 128.6, 128.9, 129.2, 137.5, 140.6, 142.8, 148.7, 149.2 (aromatic carbons).

X-ray Structural Determination. Colorless cubic crystals of **I**−**IV** were mounted in glass capillaries under an atmosphere of nitrogen in the drybox. X-ray intensity data were collected on a Siemens *P4* diffractometer, with graphite-monochromatic Mo Kα radiation (λ = 0.710 73 Å) at 21 °C, using the ω scan technique to a maximum 2θ value of 45°. Cell parameters and an orientation matrix for data collection were obtained from a least-squares analysis of the setting of up to 30 carefully centered reflections in the range of 15.0° < 2θ < 30.0°. Absorption corrections were carried out using the empirical ψ-scan method. The structures were solved by direct methods using the SHELXTL[3] package of computer programs. All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were placed at ideal positions riding on the attached carbon atoms without further refinement. Crystallographic data for all four gallium aryls are summarized in Table 1 while the molecular structures for **I**−**IV** are given in Figures 1−4, respectively.

Results and Discussion

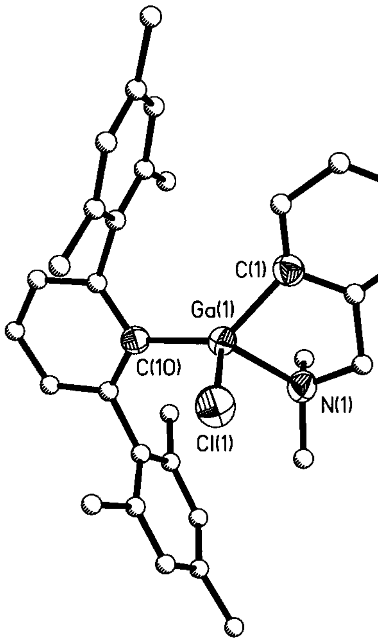

Figure 2. Molecular structure of $(Mes_2C_6H_3)[2\text{-}(Me_2NCH_2)C_6H_4]GaCl$, **II**. Selected bond distances (Å) and angles (deg): Ga−C(1) 1.991(5); Ga−C(10) 2.008(4); Ga−N 2.107(4); Ga−Cl 2.229(2); C(1)−Ga−C(10) 134.2(2); C(1)−Ga−N 84.7(2); C(10)−Ga−N 119.5(2); C(1)−Ga−Cl 103.2(2); C(10)−Ga−Cl 109.63(14); N−Ga−Cl 98.98(13).

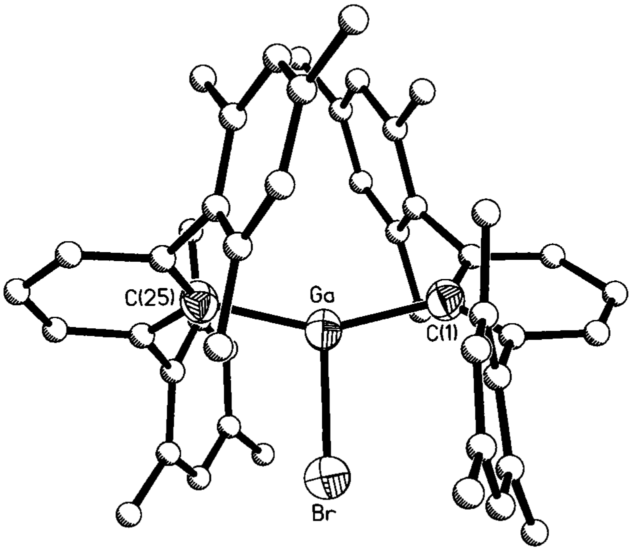

Figure 3. Molecular structure of $(Mes_2C_6H_3)_2GaBr$, **III**. Selected bond distances (Å) and angles (deg): Ga−Br 2.3183 (1); Ga−C(1) 1.988(6); Ga−C(25) 1.984(6); C(1)−Ga−C(25) 153.5(2); C(1)−Ga−Br 101.8(2); C(25)−Ga−Br 101.8(2).

During the course of this study of main group compounds containing bulky ligands, this laboratory endeavored to examine the group 13 organometallic chemistry of the sterically demanding aryl-substituted 2,6-dimesitylphenyl ligand, $Mes_2C_6H_3$. This ligand has proven to be fruitful in stabilizing interesting compounds. Particularly significant is the fact that $Mes_2C_6H_5$ was utilized by this laboratory to prepare novel sodium-[4] and potassium-based[5] cyclogallenes, $M_2[(Mes_2C_6H_3)Ga]_3$−Ga_3-based three-membered 2π-electron ring systems.[6] Central to the preparation of these complexes was bis-[(dimesitylphenyl)gallium dichloride], $[(Mes_2C_6H_3)GaCl_2]_2$, **I**, prepared and utilized *in situ* in the preparation of cyclogallenes. **I** was isolated as a discrete molecular

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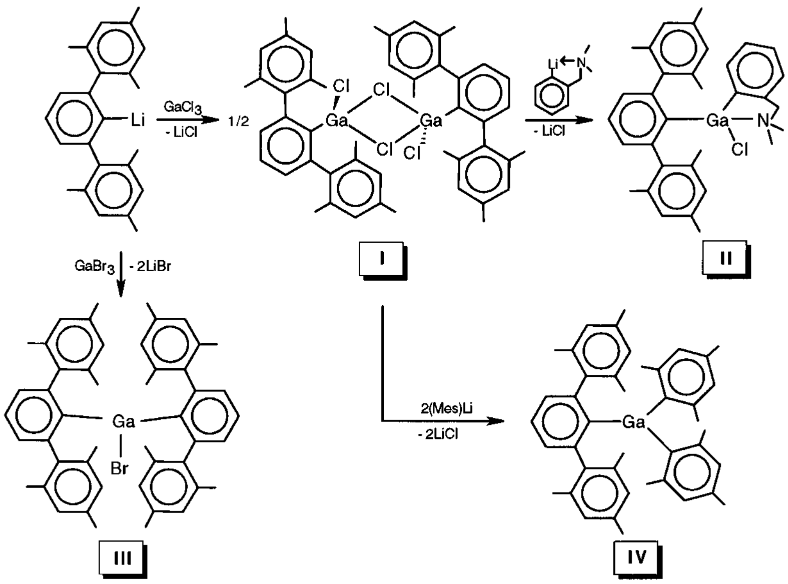
Scheme 1



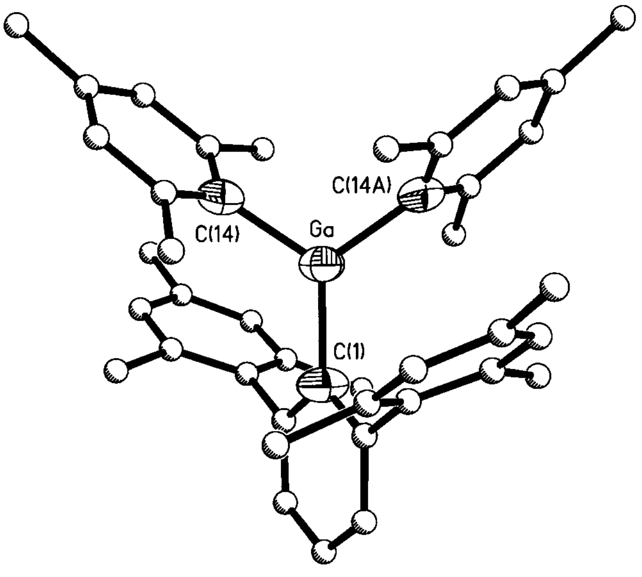


Figure 4. Molecular structure of $(Mes_2C_6H_3)(Mes)_2Ga$, **IV**. Selected bond distances (Å) and angles (deg): Ga−C(1) 1.998(7); Ga−C(14) 1.985(5); Ga−C(14a) 1.985(5); C(1)−Ga−C(14) 124.15(13); C(1)−Ga−C(14a) 124.15(14); C(14)−Ga−C(14a) 111.7(3).

complex only upon careful fractional crystallization. Reaction of **I** with $[2\text{-}(Me_2NCH_2)C_6H_4]Li$, in turn, readily affords **II** (Scheme 1). In contrast to **I**, which quickly hydrolyzes in air to give an oil-like solid, **II** is only moderately air- and moisture-sensitive.

I assumes a dimeric structure with two bridging chlorine atoms. The two bridging chlorines and two gallium atoms constitute a planar four-membered Ga_2Cl_2 ring. The two aryl ligands and the two terminal chlorines reside alternatively above and below this ring, such that the repulsion between the ligands and chlorines is minimized. As evidenced by the wide range of angles about the gallium atoms (from 86.8(2)° for Cl(4)−Ga(2)−Cl(2) to 126.0(5)° for C(25)−Ga(2)−Cl(3)), gallium adopts a seriously distorted tetrahedral geometry. The Ga−C bond distances of 1.96(2) and 1.94(2) Å agree very well with that of 1.976(6) Å in $[Mes^fGaCl_2]_2$ (Mes^f = 2,4,6-$(CF_3)_3C_6H_2$).[7] The Ga−$Cl_{bridging}$ bond lengths of 2.334(5) Å are comparable to the values of 2.323(2) and 2.328(2) Å observed in $[Mes^fGaCl_2]_2$. The Ga−$Cl_{terminal}$ bond distances of 2.172(5) Å for Ga(1)−Cl(1) and 2.287(4) Å for Ga(2)−Cl(3) are longer than those found in other organogallium dimers, such as 2.114(2) Å in $[Mes^fGaCl_2]_2$.

The propensity of 2-((dimethylamino)methyl)phenyl to serve as a bidentate ligand has long been recognized in group 13 organometallic chemistry.[8] It is well-established that this ligand readily stabilizes organometallic complexes *via* intramolecular bonding. **II** adopts a monomeric structure in which the coordination of gallium is completed by the nitrogen atom of 2-((dimethylamino)methyl)phenyl. Similar to **I**, the tetrahedral geometry in **II** is also seriously distorted by the bulky ligand, as evidenced by its four angles of gallium ranging from the most acute at 84.7(2)° for C(1)−Ga(1)−N(1) to 134.2(2)° for C(1)−Ga(1)−C(10). The Ga−C bond distances of 1.991(5) and 2.008(4) Å are slightly longer than those in **I**, indicating a more crowded environment about gallium in **II**. However, these values are comparable to those found in other four-coordinate organogallium complexes. In contrast, the Ga−Cl distance of 2.229(2) Å in **II** is much longer than those found in other tetrahedral organogallium derivatives, such as 2.1886(6) and 2.1682(6) Å for $[2\text{-}(Me_2NCH_2)C_6H_4]GaCl_2$.[9] The Ga−N distance of 2.107(4) Å compares with that of 2.071(2) Å found in $[2\text{-}(Me_2NCH_2)C_6H_4]GaCl_2$.

Bis(dimesitylphenyl)gallium bromide, $(Mes_2C_6H_3)_2GaBr$, **III**, is readily prepared by reaction of (dimesitylphenyl)lithium with gallium bromide (Scheme 1). **III**, isostructural with the previously reported chlorine

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derivative,[10] assumes a rare T-shaped geometry, as evidenced by the C−Ga−C bond angle of 153.5(2)° coupled with the C−Ga−Br bond angle of 101.8(2)° (for both C−Ga−Br angles). The Ga−C bond distances in **III** are 1.984(6) and 1.988(6) Å. The Ga−Br bond distance of 2.318(1) Å in **III** is comparable to the values of 2.324(2) and 2.331(2) Å for (i-$Pr_3C_6H_2$)GaBr[11] and (t-$Bu_3C_6H_2$)$_2$GaBr,[12] respectively.

To assess the extremes of steric loading of gallium by sterically demanding substituted phenyl ligands, **II** was allowed to interact with substituted phenyllithium reagents. Reaction of **II** with either ($Mes_2C_6H_3$)Li or [2-(Me_2NCH_2)C_6H_4]Li, in an effort to prepare ($Mes_2C_6H_3$)$_2$Ga[2-(Me_2NCH_2)C_6H_4] or ($Mes_2C_6H_3$)Ga[2-(Me_2NCH_2)C_6H_4]$_2$, respectively, proved unsuccessful, thereby suggesting that further arylation of **II** is precluded by the steric constraints of the ligands. However, an alternative strategy proved successful in further increasing the steric bulk about the gallium center of **I**. (Dimesitylphenyl)dimesitylgallium, ($Mes_2C_6H_3$)(Mes)$_2$Ga, **IV**, may be approached by either of two distinct synthetic routes. The first method concerns reaction of GaX_3 (X = Cl or Br) with 2 equiv of ($Mes_2C_6H_3$)Li followed by reaction with (Mes)Li. Alternatively, **IV** is approached by reaction of the gallium halide with 2 equiv of (Mes)Li and subsequent reaction with ($Mes_2C_6H_3$)Li. Structure and bonding characteristics for the four most closely related gallium aryls in Ph_3Ga,[13] Mes_3Ga,[14] $Mes^f{}_3Ga$ (Mes^f = 2,4,6-$(CF_3)_3C_6H_2$),[7] and (i-$Pr_3C_6H_2$)$_3$Ga[11] are conveniently compared with those of **IV**. The mean Ga−C bond distance in **IV** of 1.989(7) Å is considerably longer than that reported for Ph_3Ga (1.957 Å), Mes_3Ga (1.968(4) Å), and (i-$Pr_3C_6H_2$)$_3$Ga (1.972(11) Å), but compares well with that reported for $Mes^f{}_3Ga$ (2.001(5) Å). While the C−Ga−C bond angles sum to 360° in each of the four gallium aryls (as expected), the smallest angle in (i-$Pr_3C_6H_2$)$_3$Ga was shown to be 119.93(16)° while the values in Mes_3Ga and $Mes^f{}_3Ga$ were virtually identical at 116.6(5)° and 115.9(2)°, respectively. These values are comparable to an even smaller angle of 111.7(3)° in **IV** for C_{Mes}−Ga−C_{Mes}.

Table 2. Angles (deg) of the Aromatic Rings (Planes) about the Metal Center in (Aryl)$_3$Ga

(Aryl)$_3$Ga	Aromatic Ring Angles Relative to the GaC_3 Plane
Ph_3Ga	0, 13.2, 31.6
$Mes^f{}_3Ga$	47.0, 47.4, 54.7
Mes_3Ga	55.9
(i-$Pr_3C_6H_3$)$_3$Ga	ca. 60
($Mes_2C_6H_3$)(Mes)$_2$Ga	82.4, 82.4, 86.3

Perhaps the most interesting comparison of the gallium aryls concerns the angle of the aromatic planes relative to the plane at the GaC_3 center. The gallium aryl (i-$Pr_3C_6H_2$)$_3$Ga was characterized with high angles (ca. 60°), while in Mes_3Ga, the angle was shown to be 55.9°. The corresponding values for $Mes^f{}_3Ga$ are 54.7°, 47.4°, and 47.0°. Relative to triphenylgallium, one of the aromatic rings is coplanar with the GaC_3 plane while the angle of the remaining two aromatic rings with the plane at gallium is 13.2° and 31.6°. Indeed, the nearly flat environment at the metal center in Ph_3Ga allows for “secondary” interactions of each gallium center with the *meta*-carbon atoms of other Ph_3Ga units in the unit cell. These values, Table 2, are comparable with what must be considered dramatic values of 82.4° (for both Mes ligands) and 86.3° (for $Mes_2C_6H_3$), resulting in a nearly orthogonal arrangement of the aromatic rings about the metal center in **IV**. For perspective, the angle of the two aromatic rings in **III** form angles of 26.4° and 36.2°. This data is consistent with **IV** being the most sterically protected gallium aryl reported.

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Supporting Information Available: Text giving experimental details of the X-ray structure determination and tables of crystallographic data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates for **I**−**IV** (36 pages). Ordering information is given on any current masthead page.

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