2,6-Diphenylphenyl-Based Organometallic Compounds of Gallium†

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(2,6-Diphenylphenyl)lithium−bis(diethyl ether), $Ph_2C_6H_3Li{\cdot}2Et_2O$ (**I**), was synthesized by reaction of *n*-butyllithium with 2,6-diphenyl-1-iodobenzene in diethyl ether. Reaction of **I** with group 13 metal halides, MX_3 (M = Ga, X = Cl, I; M = In, X = Cl), affords bis(2,6-diphenylphenyl)gallium iodide, $(Ph_2C_6H_3)_2GaI$ (**II**), bis(2,6-diphenylphenyl)indium chloride, $(Ph_2C_6H_3)_2InCl$ (**III**), and bis(diethyl ether)lithium trichloro-2,6-diphenylphenylgallate, $[Li{\cdot}2Et_2O][Ph_2C_6H_3GaCl_3]$ (**IV**). Reaction of (2,4,6-triphenylphenyl)lithium with $GaCl_3$ gives (diethyl ether)lithium trichloro(2,4,6-triphenylphenyl)gallate, $[Li{\cdot}Et_2O][Ph_3C_6H_2GaCl_3]$ (**V**). The group 13 metal aryls were characterized by ^1H and ^{13}C NMR spectroscopy, elemental analyses, and single-crystal X-ray diffraction. The neutral lithium aryl (**I**) and arylgallium halide species (**II**) exhibit trigonal-planar coordination, while the coordination of the gallium atoms in anions **IV** and **V** assume distorted-tetrahedral conformations.

Introduction

The organometallic chemistry of the heavier members of group 13 has been of interest in this laboratory for some time. Considerable effort has been directed toward the preparation of low-coordination-number group 13 organometallic complexes as a function of ligand steric loading. The synthesis and structure of such group 13 metal complexes have proven to be quite interesting. In particular, the alkali-metal reduction of such complexes has been shown to yield organometallic compounds containing Ga−Ga bonds.[1−5] Herein, we report the synthesis and structural characterization of (2,6-diphenylphenyl)lithium−bis(diethyl ether), $Ph_2C_6H_3Li{\cdot}2Et_2O$ (**I**), and its utilization in the syntheses of bis(2,6-diphenylphenyl)gallium iodide, $(Ph_2C_6H_3)_2GaI$ (**II**), bis(2,6-diphenylphenyl)indium chloride, $(Ph_2C_6H_3)_2InCl$ (**III**), and bis(diethyl ether)lithium trichloro(2,6-diphenylphenyl)gallate, $[Li{\cdot}2Et_2O][Ph_2C_6H_3GaCl_3]$ (**IV**). The synthesis and structure of (diethyl ether)lithium trichloro(2,4,6-triphenylphenyl)gallate, $[Li{\cdot}Et_2O][Ph_3C_6H_2GaCl_3]$ (**V**), involving the closely related 2,4,6-triphenylphenyl ligand, is also reported (Scheme 1).

Experimental Section

General Comments. Standard Schlenk techniques were employed in conjunction with an inert-atmosphere drybox (M Braun Labmaster 130). Solvents were distilled under a nitrogen atmosphere with sodium benzophenone. Nitrogen was passed through copper-based purification and molecular sieve drying columns prior to use. Gallium(III) chloride, gallium(III) iodide, indium(III) chloride, bromobenzene, 1,3,5-triphenylbenzene, *n*-butyllithium, and bromine were purchased from Aldrich Chemical Co. (Milwaukee, WI), while 2,6-dibromoaniline was purchased from Lancaster Synthesis Inc. (Windham, NH). 2,6-Diphenyl-1-iodobenzene, $Ph_2C_6H_3I$, was prepared according to the published procedure.[6] Elemental analyses were performed by E + R Microanalytical Laboratories (Parsippany, NJ). NMR spectra were recorded on a Bruker AC-300 or Bruker AC-250 spectrometer. X-ray intensity data were collected on a Siemens *P4* diffractometer (50kV/40mA).

Synthesis of $Ph_2C_6H_3Li{\cdot}2Et_2O$ (I). To a suspension of 2,6-diphenyl-1-iodobenzene (30 g, 86 mmol) in degassed hexane (150 mL) was added *n*-butyllithium (60 mL of a 1.6 M solution in hexanes) via syringe at room temperature over a period of 10 min. The inert nitrogen atmosphere was rigorously maintained throughout the procedure. The solution was stirred for 24 h, after which it was cooled to −78 °C for 3 h and filtered. The remaining white powder was washed with another 150 mL portion of degassed hexane. The fine crude product was then dried under vacuum and extracted with diethyl ether. Cooling the ether solution to −25 °C afforded colorless rod-shaped crystals (24.2 g, 63 mmol). X-ray-quality crystals were grown from a saturated ether solution at room temperature, undisturbed on the benchtop for 2 days. Yield: 73%. Mp: 181 °C. Anal. Calcd (found) for $Ph_2C_6H_3Li{\cdot}2Et_2O$: C, 81.25 (80.69); H, 8.78 (8.50). ^1H NMR (300 MHz, 298 K, THF-d_8): δ 1.13 (m, 12H), $-OCH_2CH_3$; 3.33 (m, 8H), $-OCH_2CH_3$; 6.93 (t, 2H), *p′*-C*H*; 7.10 (t, 4H), *m′*-C*H*; 7.25 (d, 4H), *o′*-C*H*; 7.43 (t, 1H), *p*-C*H*; 7.67 (d, 2H), *m*-C*H*. ^{13}C NMR (300 MHz, 298 K, THF-d_8): δ 18.3, $-OCH_2CH_3$; 68.5, $-OCH_2CH_3$; 125.2, *m*-CH; 126.3, *p′*-CH; 129.0, *o′*-CH; 130.5, *m′*-CH; 131.1, *p*-CH; 147.8, *i′*-*C*; 152.2, *o*-*C*; 175.0, *i*-*C*.

Synthesis of $(Ph_2C_6H_3)_2GaI$ (II). A solution of (2,6-diphenylphenyl)lithium (2.36 g, 10 mmol) in diethyl ether (30 mL) was added to a solution of GaI_3 (2.25 g, 5 mmol) in diethyl

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† Dedicated to Prof. Dr. Peter Jutzi on the ocassion of his 60th birthday.

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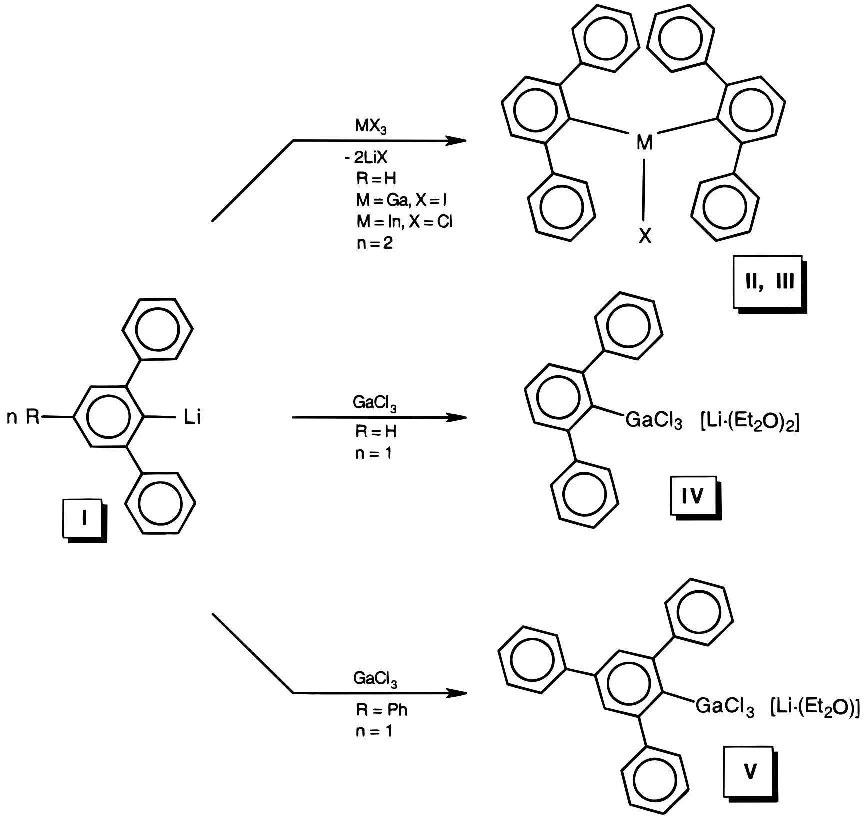
Scheme 1



ether (30 mL) at −78 °C. The reaction mixture was stirred for 3 h and then warmed to room temperature. The reaction mixture was stirred for an additional 48 h, after which a yellow solution resulted with a white precipitate (LiI). Upon filtration and subsequent cooling to −25 °C for 1 week, colorless crystals were obtained. Recrystallization from toluene yielded X-ray-quality crystals (2.29 g, 3.5 mmol). Yield: 71%. Mp: 214.5−215.5 °C. Anal. Calcd (found) for $(Ph_2C_6H_3)_2GaI$: C, 65.99 (65.70); H, 4.00 (3.85). ^1H NMR (300 MHz, 298 K, THF-d_8): δ 7.20 (t, 4H), *p*′-C*H*; 7.25 (t, 8H), *m*′-C*H*; 7.34 (d, 8H), *o*′-C*H*; 7.57 (t, 2H), *p*-C*H*; 7.69 (d, 4H), *m*-C*H*. ^{13}C NMR (300 MHz, 298K, THF-d_8): δ 130.5, *m*-*C*H; 131.0, *p*′-*C*H; 132.0, *m*′-*C*H; 132.5, *p*-*C*H; 133.2, *o*′-*C*H; 145.0, *i*′-*C*; 148.8, *o*-*C*; 154.2, *i*-*C*.

Synthesis of $(Ph_2C_6H_3)_2InCl$ (III). A solution of (2,6-diphenylphenyl)lithium (2.36 g, 10 mmol) in diethyl ether (30 mL) was added to a solution of $InCl_3$ (1.10 g, 5 mmol) in diethyl ether (30 mL) at −78 °C. The reaction mixture was stirred for 3 h and then warmed to room temperature. The reaction mixture was stirred for an additional 72 h, after which a yellow solution with a white precipitate (LiCl) resulted. Upon filtration and subsequent cooling to −25 °C for 1 week, colorless cubic crystals were obtained (2.55 g, 3.9 mmol). Yield: 78%. Mp: 210.4 °C. Anal. Calcd (found) for $(Ph_2C_6H_3)_2InCl$: C, 71.04 (70.88); H, 4.27 (4.15). ^1H NMR (300 MHz, 298 K, THF-d_8): δ 7.17 (t, 4H), *p*′-C*H*; 7.22 (t, 8H), *m*′-C*H*; 7.31 (d, 8H), *o*′-C*H*; 7.51 (t, 2H), *p*-C*H*; 7.67 (d, 4H), *m*-C*H*. ^{13}C NMR (300 MHz, 298K, THF-d_8): δ 130.2, *m*-*C*H; 130.7, *p*′-*C*H; 131.6, *m*′-*C*H; 132.4, *p*-*C*H; 132.9, *o*′-*C*H; 144.5, *i*′-*C*; 148.5, *o*-*C*; 153.9, *i*-*C*.

Synthesis of $[Li{\cdot}2Et_2O][Ph_2C_6H_3GaCl_3]$ (IV). A solution of (2,6-diphenylphenyl)lithium (2.36 g, 10 mmol) in diethyl ether (30 mL) was added to a solution of $GaCl_3$ (1.71 g, 10 mmol) in diethyl ether (30 mL) at −78 °C. The reaction mixture was stirred for 3 h and then warmed to room temperature. The reaction mixture was stirred for an additional 48 h, after which a yellow solution with a minute amount of white precipitate (LiCl) resulted. Filtration and subsequent cooling to −25 °C for 2 days yielded colorless crystals. Recrystallization from diethyl ether yielded X-ray-quality crystals (3.81 g, 6.8 mmol). Yield: 68%. Mp: 96.1−96.9 °C. Anal. Calcd (found) for $[Li{\cdot}2Et_2O][Ph_2C_6H_3GaCl_3]$: C, 55.71 (55.11); H, 5.94 (5.52). ^1H NMR (300 MHz, 298 K, THF-d_8): δ 1.11 (m, 12H), $-OCH_2CH_3$; 3.36 (m, 8H), $-OCH_2CH_3$; 7.27 (t, 2H), *p*′-C*H*; 7.32 (t, 4H), *m*′-C*H*; 7.35 (d, 4H), *o*′-C*H*; 7.42 (t, 1H), *p*-C*H*; 7.60 (d, 2H), *m*-C*H*. ^{13}C NMR (300 MHz, 298 K, THF-d_8): δ 18.2, $-OCH_2CH_3$; 68.8, $-OCH_2CH_3$; 129.3, *m*-*C*H; 130.4, *p*′-*C*H; 130.7, *m*′-*C*H; 131.12, *i*′-*C*; 131.4, *p*-*C*H; 133.4, *o*′-*C*H; 149.7, *o*-*C*; 154.6, *i*-*C*.

Synthesis of $[Li{\cdot}Et_2O][Ph_3C_6H_2GaCl_3]$ (V). A solution of $Ph_3C_6H_2Li{\cdot}2Et_2O$ (3.68 g, 8.0 mmol) in diethyl ether (45 mL) was added dropwise over a period of 10 min to a solution of $GaCl_3$ (1.41 g, 8.0 mmol) in diethyl ether (20 mL) at −78 °C. The reaction mixture was stirred for 3 h, warmed to room temperature, and then stirred for an additional 30 h. A clear yellow solution resulted along with a small amount of precipitate (LiCl). After filtration, the solution was concentrated and then cooled to −25 °C for 24 h. This afforded colorless X-ray-quality crystals (2.31 g; 4.10 mmol). Yield: 52%. Mp: 97.3−98.0 °C. Anal. Calcd (found) for $[Li{\cdot}Et_2O][Ph_3C_6H_2GaCl_3]$: C, 60.37 (59.13); H, 5.85 (5.73). ^1H NMR (250 MHz, 298 K, THF-d_8): δ 1.00 (t, 6H), $-OCH_2CH_3$; 3.28 (q, 4H), $-OCH_2CH_3$; 7.22 (t, 1H), *p*″-C*H*; 7.26 (t, 2H), *p*′-C*H*; 7.34 (t, 2H), *m*″ −C*H*; 7.37 (t, 4H), *m*′-C*H*; 7.56 (d, 2H), *o*″-C*H*; 7.59 (d, 4H), *o*′-C*H*; 7.74 (s, 2H), *m*-C*H*. ^{13}C NMR (250 MHz, 298 K, THF-d_8): δ 15.8, $-OCH_2CH_3$; 66.4, $-OCH_2CH_3$; 125.7, *m*-*C*H; 126.9, *o*″-*C*H; 127.3, *p*″-*C*H; 128.0, *o*′-*C*H; 128.4, *p*′-*C*H; 129.5, *m*″-*C*H; 129.6, *m*′-*C*H; 131.1, *p*-*C*; 142.1, *i*″-*C*; 143.3, *i*′-*C*; 147.2, *o*-*C*; 152.7, *i*-*C*.

Crystal Structure Determination. Colorless crystals of **I**, **II**, **IV**, and **V** 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-monochromated 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 settings of up to 30 carefully centered reflections in the range 15.0° < 2θ

Table 1. Crystallographic Data

	$Ph_2C_6H_3Li{\cdot}2Et_2O$ (**I**)	$(Ph_2C_6H_3)_2GaI$ (**II**)	$[Li{\cdot}2Et_2O][Ph_2C_6H_3GaCl_3]$ (**IV**)	$[Li{\cdot}Et_2O][Ph_3C_6H_2GaCl_3]$ (**V**)
empirical formula	$C_{26}H_{33}LiO_2$	$C_{36}H_{26}GaI$	$C_{26}H_{33}GaCl_3LiO_2$	$C_{28}H_{27}GaCl_3LiO$
fw	384.46	608.22	560.53	562.51
color, habit	colorless, cubic	colorless, cubic	colorless, cubic	colorless, cubic
space group	monoclinic, $C2/c$ (No. 15)	orthorhombic, $Pbcn$ (No. 60)	monoclinic, $P2_1/n$ (No. 14)	triclinic, $P\bar{1}$(No. 2)
unit cell dimens				
a (Å)	14.633(4)	16.781(3)	11.024(3)	9.377(3)
b (Å)	13.965(3)	12.480(2)	16.861(3)	10.807(4)
c (Å)	12.569(3)	13.763(3)	15.928(3)	18.339(5)
α (deg)				85.70(2)
β (deg)	110.36(3)		100.99(2)	78.51(2)
γ (deg)				69.00(3)
formula units/cell	4	4	4	2
V (Å^3)	2408.2(11)	2882(10)	2906.5(10)	1700.3(9)
D_{calcd} (g/cm^3)	1.060	1.510	1.281	1.099
no. of unit cell rflns	25	30	30	30
maximum 2θ angle (deg)	45	50	50	50
no. of unique rflns	1333	9434	7402	2364
no. of obsd rflns ($I > 2\sigma(I)$)	1333	2246	3842	2364
no. of params refined		174	299	279
abs coeff (mm^{-1})	0.064	2.048	1.241	1.060
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 = 0.056 wR2 = 0.143	R1 =0.042 wR2 = 0.130	R1 = 0.067 wR2 = 0.183	R1 = 0.085 wR2 = 0.240
R indices (all data)	R1 = 0.102 wR2= 0.170	R1 = 0.068 wR2 = 0.170	R1 = 0.119 wR2 = 0.251	R1 = 0.106 wR2 = 0.267
goodness of fit, S	1.057	1.113	1.687	1.134
largest diff peak (e/Å^3)	0.149	0.488	0.683	0.816

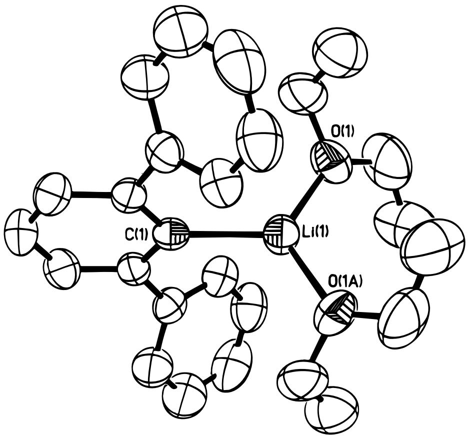


Figure 1. Molecular structure of $Ph_2C_6H_3Li{\cdot}2Et_2O$ (**I**). Selected bond distances (Å) and angles (deg): Li(1)−C(1), 2.106(9); Li(1)−O(1), 1.943(5); O(1)−C(11), 1.461(4); O(1)−C(13), 1.394(5); C(1)−Li(1)−O(1), 120.8(2); O(1)−Li(1)−O(1a), 118.4(4); C(11)−O(1)−C(13), 114.6(3); C(11)−O(1)−Li(1), 112.3(3).

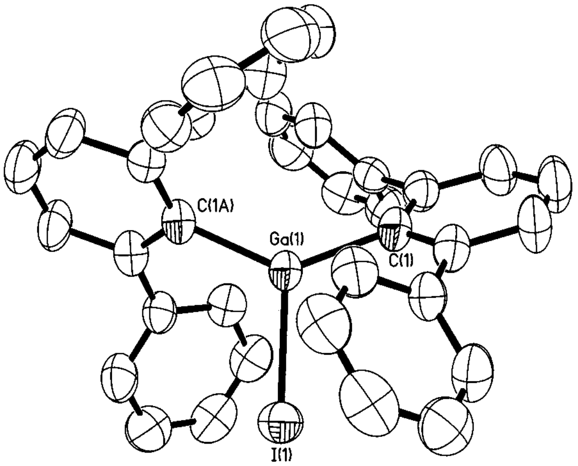


Figure 2. Molecular structure of $(Ph_2C_6H_3)_2GaI$ **(II)**. Selected bond distances (Å) and angles (deg): Ga(1)−C(1), 1.971(12); Ga(1)−C(19), 1.971(12); Ga(1)−I(1), 2.550(1); C(1)−Ga(1)−C(1a), 134.3(3); C(1)−Ga(1)−I(1), 112.86(1); C(1a)−Ga(1)−I(1), 112.86(1).

< 30.0°. Absorption corrections were carried out using the empirical ψ-scan method. The structures were solved by direct methods using the SHELXTL 5.0[7] 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 compounds **I, II, IV,** and **V** are summarized in Table 1, while the molecular structures are given in Figures 1-4, respectively.

Results and Discussion

Organolithium compounds have assumed a central role in synthetic organometallic chemistry. In comparison to traditional Grignard reagents, organolithium reagents frequently offer enhanced synthetic flexibility.[8] While much is known about alkyl- and alkylsilyl-substituted aryllithium compounds, sterically crowded derivatives having two phenyl rings at the ortho positions of the central ring of the lithium aryl have been attracting increasing attention.

Sterically bulky aryl ligands have demonstrated great utility in the synthesis of organometallic complexes with unique bonding and coordination. Several striking examples which clearly depict the stabilizing capacity of sterically encumbered aryls have been recently reported. (2,6-Dimesitylphenyl)lithium has been characterized as being dimeric, $[Mes_2C_6H_3Li]_2$ (Mes = 2,4,6-

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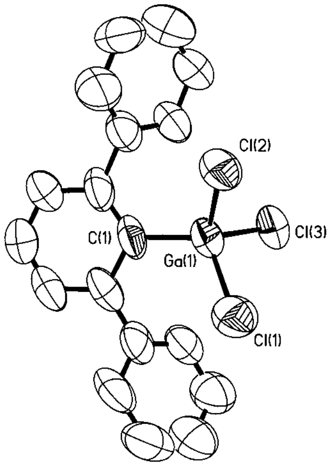

Figure 3. Molecular structure of $[Ph_2C_6H_3GaCl_3]^-$ (anion of **IV**). Selected bond distances (Å) and angles (deg): Ga(1)−C(1), 1.968(14); Ga(1)−Cl(1), 2.244(5); Ga(1)−Cl(2), 2.249(5); Ga(1)−Cl(3), 2.206(5); Li(1)−O(1), 1.934(5); O(1)−C(20), 1.731(8); O(1)−C(21), 1.353(5); Li(1)−O(2), 1.913(4); O(2)C(23), 1.46(2); O(2)−C(25), 1.45(4); C(1)−Ga(1)−Cl(1), 117.8(6); C(1)−Ga(1)−Cl(2), 113.3(5); C(1)−Ga(1)−Cl(3), 115.0(5); Cl(1)−Ga(1)−Cl(2), 96.07(18); C(1)−Ga(1)−Cl(3), 104.9(2); C(3)−Ga(1)−Cl(2), 107.68(19).

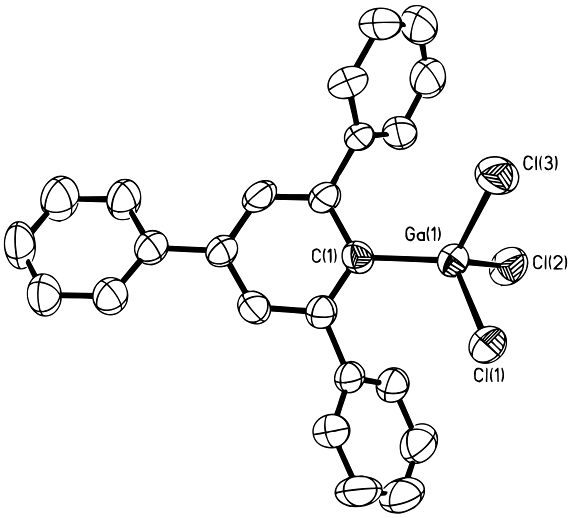

Figure 4. Molecular structure of $[Ph_3C_6H_2GaCl_3]^-$ (anion of **V**). Selected bond distances (Å) and angles (deg): Ga(1)−C(1), 1.972(11); Ga(1)−Cl(1), 2.253(3); Ga(1)−Cl(2), 2.246(4); Ga(1)−Cl(3), 2.180(4); Li(1)−O(1), 2.02(4); O(1)−C(25), 1.96(3); O(1)−C(27), 1.43(3); C(1)−Ga(1)−Cl(1), 113.6(3); C(1)−Ga(1)−Cl(2), 115.6(3); C(1)−Ga(1)−Cl(3), 119.4(3); Cl(1)−Ga(1)−Cl(2), 95.28(14); C(1)−Ga(1)−Cl(3), 103.1(2).

Table 2. Bond Distances (Å) in Ether-Solvated Lithium Aryls

compd	Li−C	ref
$(PhLiEt_2O)_4$	2.31(4)	14
$[MesLi(THF)_2]_2$	2.271(3)	15
$(2,4,6\text{-}i\text{-}Pr_3C_6H_2)Li(Et_2O)_2$	2.203(3)	16
$Ph_2C_6H_3Li(Et_2O)_2$	2.106(9)	this work
$Ph_3C_6H_2Li(Et_2O)_2$	2.08(2)	13a
	2.074(16)	13b
$(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3Li(Et_2O)$	2.017(7)	12

Table 3. Angles (deg) of Ortho Aromatic Rings (Planes) Relative to the Central Aromatic Ring

compd	angle	ref
$Ph_2C_6H_3Li(Et_2O)_2$	60.0	this work
$[Mes_2C_6H_3Li]_2$	90.0	9
$2,6\text{-}(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3Li(Et_2O)$	77.3, 76.1	12

$Me_3C_6H_2$),[9] and has been employed in reaction with GaX_3 (X = Cl, Br) to afford the rare T-shaped complexes $(Mes_2C_6H_3)_2GaX$ (X = Cl,[10] Br[11]). The sterically crowded 2,6-dimesitylphenyl ligand was also utilized in the synthesis and isolation of cyclogallenes, $M_2[Mes_2C_6H_3Ga]_3$ (M = Na, K).[1,2,5] These interesting compounds contain a dianionic three-membered ring composed of the three gallium atoms and exhibit *metalloaromaticity*. Further substitution of the ortho aryl groups of the lithium aryl has proven successful as well. 2,6-Bis(triisopropylphenyl)phenyllithium has been structurally characterized as a monomer of the formula $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3Li{\cdot}Et_2O$.[12] This extremely crowded *m*-terphenyl-based ligand has been employed in the preparation of unusual compounds containing Ga−Ga[3] and Ga−Fe[4] bonds. A corresponding example of a main-group organometallic complex stabilized by an unsubstituted terphenyl ligand, namely 2,6-diphenylphenyl, is conspicuously absent.

The synthesis of (2,6-diphenylphenyl)lithium−bis(diethyl ether), $Ph_2C_6H_3Li{\cdot}2Et_2O$ (**I**), was approached in a straightforward manner by reaction of 2,6-diphenyl-1-iodobenzene with *n*-butyllithium. Subsequent recrystallization from diethyl ether yielded the product as colorless rods. The structure of the compound was determined by single-crystal X-ray diffraction. The complex, an example of a monomeric lithium aryl, exhibits the lithium metal center in a trigonal-planar coordination environment. The Li(1)−C(1) bond distance of 2.106(9) Å is longer than the Li−C bond of 2.08(2) Å found in the closely related lithium aryl (2,4,6-triphenylphenyl)lithium−bis(diethyl ether), $Ph_3C_6H_2Li{\cdot}2Et_2O$.[13] A comparison of Li−C bond distances of other known ether-solvated lithium aryls is given in Table 2.

An interesting comparison may also be made between **I** and related lithium aryls by considering the angles of the planes of the ortho rings relative to the plane of the central ring.[14−16] In the excessively bulky isopropyl derivative $2,6\text{-}(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3Li{\cdot}Et_2O$, the planes of the $2,4,6\text{-}i\text{-}Pr_3C_6H_2$ aryl rings are 77.3 and 76.1° relative to the plane of the central C_6H_3 ring.[12] In $[Mes_2C_6H_3Li]_2$, the planes of the mesityl rings are perpendicular (ca. 90°) to the plane of the central ring, while in **I** the ortho phenyl rings are in planes at 60.0° relative to the central ring (Table 3).

Investigation of the 2,6-diphenylphenyl ligand was undertaken in an effort to gain further insight into the significance of substitution of the ortho phenyl rings when employing sterically crowding *m*-terphenyl-based ligands. The first organometallic compounds to incor-

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porate 2,6-diphenylphenyl as a ligand, reported herein, provide evidence of the effects of substitution on structure and bonding in group 13 metal aryls. An examination of the bond distances of $(Ph_2C_6H_3)_2GaI$, **II**, reveals a Ga−I distance of 2.550(1) Å and an independent Ga−C distance of 1.980(12) Å. The Ga−I bond in **II** (2.550(1) Å) is slightly shorter than the Ga−I bond distances (2.593(2) and 2.582 (2) Å) in $[Mo(\eta^5\text{-}C_5H_4Me)(CO)_3GaI_2\cdot Et_2O]$.[17] Inspection of the C(1)−Ga−C(1a) bond angle of **II** reveals an angle of 134.3(3)°. Comparison to the C−Ga−C linkage in the previously reported arylgallium halides $(Mes_2C_6H_3)_2GaX$ (X = Cl,[10] Br[11]) offers a striking contrast. While the large C−Ga−C bond angles of 153.5(5) and 153.3° in the chloride and bromide, respectively, allowed the coordination environment about the gallium centers to be described as T-shaped, the corresponding angle in compound **II**, smaller by almost 20°, requires the coordination to be described as trigonal planar (albeit somewhat distorted). The corresponding indium compound bis(2,6-diphenylphenyl)indium chloride, $(Ph_2C_6H_3)_2InCl$ (**III**), has been prepared as well and characterized by elemental analysis and ^1H and ^{13}C NMR. Even though structural data for **III** are not presented herein (repeated attempts by this laboratory to obtain X-ray-quality crystals of **III** were unsuccessful), structural features of **III** are expected to be quite similar to those observed for **II**.

Consideration of the structures of $[Li\cdot 2Et_2O][Ph_2C_6H_3GaCl_3]$ (**IV**) and $[Li\cdot Et_2O][Ph_3C_6H_2GaCl_3]$ (**V**) provide an interesting contrast to the gallium aryl discussed above. **IV** and **V** display the gallium centers in four-coordinate distorted-tetrahedral geometry. The gallium anions are monomeric and are coordinated to a $Li\cdot nEt_2O$ cation ($n = 2$ for **IV**, $n = 1$ for **V**). The Ga−Cl bond distances in **IV** and **V** are quite similar and generally unremarkable. Two other organometallic compounds of group 13 involving the 2,4,6-triphenylphenyl ligand have been reported: $[(Ph_3C_6H_2)GaP(\text{cyclo-}C_6H_{11})]_3$[18] and $(Ph_3C_6H_2)AlBr_2(Et_2O)$.[19] While the conformation of the 2,4,6-triphenylphenyl ligand in these two compounds compares well to that in **V**, the Ga−C bond distances in $[(Ph_3C_6H_2)GaP(\text{cyclo-}C_6H_{11})]_3$ (2.004(9) Å, 1.992(11) Å, and 2.019(13) Å) are slightly longer than that observed for **V** (1.972(11) Å).

The literature reveals only one similar reported structure, $[i\text{-}Pr_3C_6H_2GaCl_3Li\cdot Et_2O]_2$, which is dimeric and features two chlorine atoms μ_2-bridging the Li^+ ion.[20] Metrical values observed in **IV** and **V** correspond well with those reported for this compound. The Li−Cl interatomic distances for **IV** and **V** are well beyond reported Li−Cl bond distances.[21] The $[i\text{-}Pr_3C_6H_2GaCl_3\text{-}Li\cdot Et_2O]_2$ complex is easily compared to the recently reported $[(Mes_2C_6H_3)AlBr_3Li]_2$ compound—a loosely associated Li_2Br_4 octahedrally stabilized organoaluminum bromide dimer.[22] It is interesting to note that analogous syntheses employing the more sterically crowding $Mes_2C_6H_3$ and $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3$ lithium salts in equimolar reactions with MCl_3 (M = Ga, In) have afforded the dimeric species $[Mes_2C_6H_3GaCl_2]_2$,[11] $[Mes_2C_6H_3InCl_2]_2$,[23] and $[(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3MCl_2]_2$[24] (M = Ga, In) with the group 13 metal featuring distorted-tetrahedral coordination. Clearly, striking structural changes are achieved by employing nonsubstituted *m*-terphenyl-based ligands such as 2,6-diphenylphenyl and the similar 2,4,6-triphenylphenyl, thereby providing evidence in support of the significance of steric loading on structure and bonding in the organometallic chemistry of the group 13 metals.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, positional parameters, and bond distances and angles (31 pages). Ordering information is given on any current masthead page.

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