

Intramolecularly Base-Stabilized Group 13 Aryloxy Complexes

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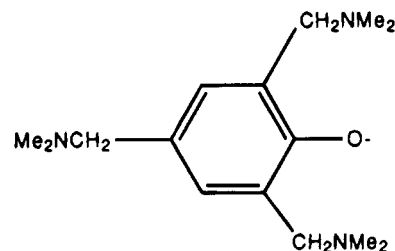
Three group 13 complexes of the *ortho*-chelating 2,4,6-tris((dimethylamino)methyl)phenoxy (Ar^{O^-}) ligand have been prepared. Reaction of the lithio derivative, $\text{Ar}^{\text{O}}\text{Li}$, with gallium trichloride in 1:1 stoichiometry afforded $[\text{Ar}^{\text{O}}\text{GaCl}_2]_2$ (**1**). Treatment of gallium or indium trichloride with 2 equiv of $\text{Ar}^{\text{O}}\text{Li}$ resulted in the gallate and indate complexes $[(\text{Ar}^{\text{O}})_2\text{GaCl}_2]\text{Li}$ (**2**) and $[(\text{Ar}^{\text{O}})_2\text{InCl}_2]\text{Li}$ (**3**), respectively. Compound **2** was also prepared by addition of 1 equiv of $\text{Ar}^{\text{O}}\text{Li}$ to **1**. The structure of the indate complex, **3**, has been determined by X-ray crystallography. Compound **3** crystallizes in the monoclinic space group $C2/c$ with $a = 14.903(3)$ Å, $b = 14.936(3)$ Å, $c = 22.076(4)$ Å, $\beta = 101.78(3)^\circ$, $V = 4810(2)$ Å³, and $Z = 4$. All three compounds were characterized on the basis of elemental analysis, NMR, and mass spectral data.

Introduction

As part of our continuing interest in unusual structures and bonding in main-group element chemistry, we have recently explored the utility of the *ortho*-chelating amine ligand, 2,6-bis((dimethylamino)methyl)phenyl first introduced by van Koten and co-workers.¹ Examples of novel main-group species that have been stabilized by the use of this ligand include group 15 halide complexes,² diphospha- and diarsadigallectanes,^{3,4} group 13 intermetallic derivatives,⁵ and monomeric group 13 dihydride complexes.⁶ Significant developments in other laboratories include the isolation and structural characterization of complexes of lithium,⁷ tin,^{7,10} gallium,⁸ and indium.^{8,9} Given the usefulness of this aryl "pincer" ligand, we have become interested in exploring the consequences of employing an aryloxy analogue with potentially chelating aminomethyl arms. In the context

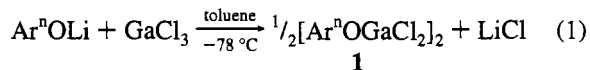
of main-group chemistry, ligands of this type have only been employed for the synthesis of lithium and sodium derivatives.¹¹

In the present publication, we explore the use of the 2,4,6-tris((dimethylamino)methyl)phenoxy ligand, $[\text{Ar}^{\text{O}}]^-$, for the preparation of the following gallium and indium compounds: $[\text{Ar}^{\text{O}}\text{GaCl}_2]_2$ (**1**) and $[(\text{Ar}^{\text{O}})_2\text{MCl}_2]\text{Li}$, where $\text{M} = \text{Ga}$ (**2**) and In (**3**).



Results and Discussion

Synthesis and Characterization. The neutral gallium dichloride $[\text{Ar}^{\text{O}}\text{GaCl}_2]_2$ (**1**) was prepared in good yield (75%) by the metathetical reaction of 1 equiv of the lithio aryloxy, $\text{Ar}^{\text{O}}\text{Li}$, with GaCl_3 according to eq 1. Unfortunately, crystals



of **1** were not suitable for X-ray diffraction study. However, the empirical composition of **1** is in accord with elemental analysis data (Experimental Section), and the dimeric nature of **1** was established on the basis of mass spectral data (HRMS). In the ¹H NMR of **1**, the *para* and *ortho* NMe_2 groups appear as singlets at δ 2.16 and 2.19 respectively. The methylene groups for both the *para* and *ortho* CH_2NMe_2 groups appear as a singlet at δ 3.40. These NMR chemical shifts are similar to those found for $[(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{GaCl}_2$.³ Proton NMR equivalence of *ortho* and *para* CH_2NMe_2 groups was also found for **3**. In this case, the structure was established by X-ray analysis (*vide infra*). Similar observations have been made with other complexes. For example, the diphosphadigallectane $\{[(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{GaPSiPh}_3\}_2$ exhibits equivalence of the NMe_2 groups (δ 2.32 (s)) in solution, yet the crystal structure

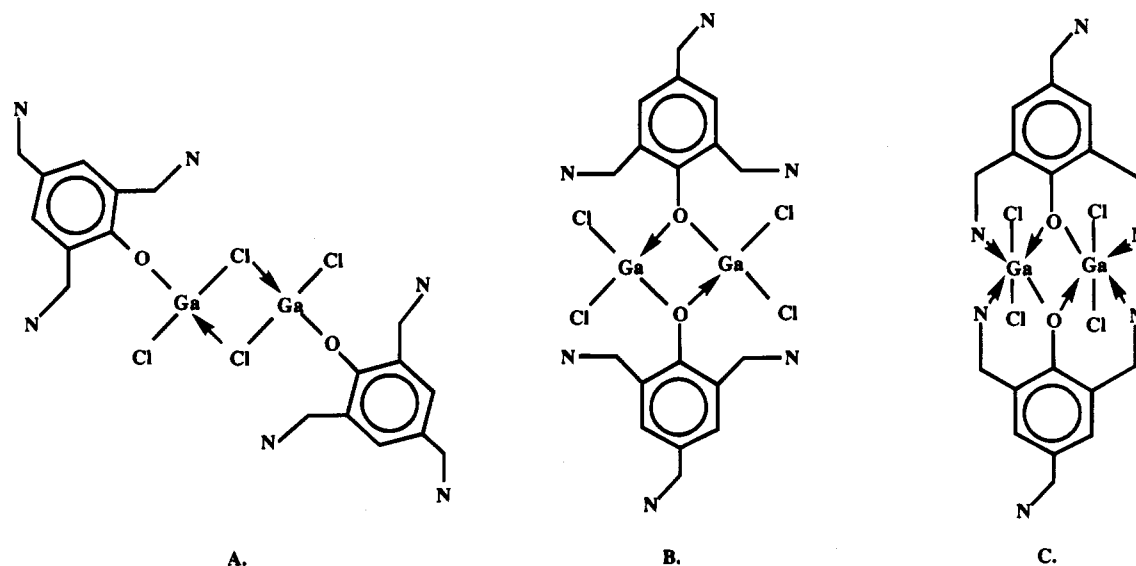
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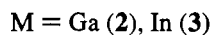
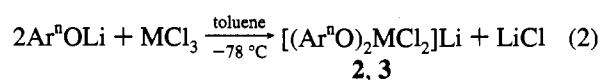
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Chart 1. Possible Structures for **1** (*N*-Me Groups Omitted for Clarity)

featured two distinct CH_2NMe_2 environments. There are three possible structures (Chart 1) that are consistent with the NMR and mass spectral data. Alkylgallium chloride complexes are well-known to adopt dimeric halide-bridged structures (A). This is the case, for example, for such structurally characterized complexes as $[\textit{t}\text{-BuGaCl}_2]_2$,¹² $[(\text{C}_6\text{H}_{11})_2\text{GaCl}]_2$,¹² $[\text{Me}_5\text{C}_5\text{-GaCl}_2]_2$,¹³ and $[(\text{Me}_5\text{C}_5)_2\text{GaCl}]_2$.¹³ However, aryloxide ligands can also support bonding arrangements in which the oxygen atoms bridge the two metal centers as shown in B and C. In fact, the preference for bridging heteroatoms (N, O, P, etc.) over bridging chlorides in sterically unencumbered gallium and indium complexes is a well-established trend. Examples include $[\text{NMe}_2(\mu\text{-NMe}_2)\text{GaCl}]_2$,¹⁴ $[\text{TMP}(\mu\text{-OEt})\text{GaCl}]_2$ ¹⁴ (TMP = (2,2,6,6-tetramethylpiperide), and $[(\mu\text{-P}(\text{SiMe}_3)_2)\text{GaCl}]_2$.¹⁵ Given this trend, the preferred structure for **1** is C. Moreover, this structure is similar to that found for the anionic species **3** by X-ray crystallography (*vide infra*).

High yields (>80%) of the ionic complexes **2** and **3** were isolated from the reaction of two equivalents of Ar^nOLi with the metal trichloride in toluene solution according to eq 2. Both complexes are stable in air for a few hours.



The proposed formulas for **2** and **3** are in accord with elemental analysis data. The presence of the gallate anion $[(\text{Ar}^n\text{O})_2\text{GaCl}_2]^-$ was evident in the CI (negative) mass spectrum. In the case of **3**, the CI mass spectrum exhibited a peak at *m/e* 720 corresponding to $[(\text{Ar}^n\text{O})_2\text{InCl}_2]\text{Li}$. Interestingly, repeated attempts to detect this peak by HRMS resulted in the detection of a peak corresponding to the bis(aryloxy)indium chloride, thus indicating that, under mass spectral conditions, the lithium indate decomposes rapidly to the $(\text{Ar}^n\text{O})_2\text{InCl}$

Table 1. X-ray Structure Determination Data for $\text{Li}[(\text{Ar}^n\text{O})_2\text{InCl}_2]\cdot 2\text{toluene}$ (**3**)

formula	$\text{C}_{44}\text{H}_{68}\text{Cl}_2\text{-InLiN}_6\text{O}_2$	<i>hkl</i> range	<i>h</i> = -1 to +15; <i>k</i> = -1 to +15; <i>l</i> = -23 to +23
<i>M</i>	905.70		
cryst syst	monoclinic	total no. of reflns	3404
space group	<i>C2/c</i>	no. of unique reflns	2792
<i>a</i> (Å)	14.903(3)	significance test	$F_\sigma > 4\sigma(F_\sigma)$
<i>b</i> (Å)	14.936(3)	No. of obsd reflns	2358
<i>c</i> (Å)	22.076(4)	no. of refined params	267
β (deg)	101.78(3)	weighting chart	0.0008
<i>V</i> (Å ³)	4810(2)	param <i>g</i> in $w = 1/[\sigma^2(F_\sigma) + gF_\sigma^2]$	
<i>Z</i>	4		
<i>D_c</i> (g cm ⁻³)	1.251	final <i>R</i>	0.0575
<i>F</i> (000)	1904	final <i>R_w</i>	0.0772
μ (cm ⁻¹)	6.41		

species. Several attempts were made to isolate the latter compound by refluxing **3** in toluene solution. The resulting white solid consisted of LiCl, traces of $(\text{Ar}^n\text{O})_2\text{InCl}$, and another product that has not yet been identified. The filtrate from this reaction contained a small amount of the anionic species as confirmed by melting point determination and mass spectral analysis. Future work is aimed at isolating discrete bis(aryloxy) metal halide species that do not incorporate lithium chloride. In the ¹H NMR spectra, the NMe₂ chemical shifts for **2** and **3** are identical and appear as singlets at δ 2.20 for the *ortho* substituents and δ 2.17 for the *para* substituents. However, the CH_2NMe_2 groups do exhibit slight chemical shift differences: δ 3.37 (*o*) and 3.49 (*p*) for **2**, and 3.36 (*o*) and 3.45 (*p*) for **3**.

X-ray Crystal Structure of $\text{Li}[(\text{Ar}^n\text{O})_2\text{InCl}_2]$ (3**).** Individual molecules of **3** crystallize in the centrosymmetric space group *C2/c* with four molecules in the unit cell. A summary of X-ray structure determination data is given in Table 1. Relevant bond lengths and angles are assembled in Table 2 and positional parameters are presented in Table 3. The molecular structure and atom numbering chart are shown in Figure 1. Two molecules of toluene are present as solvent of crystallization and are >3.6 Å from the central indate anion. The overall structure of the complex is such that a crystallographic *C*₂ axis passes through the indium and lithium atoms. The two Ar^nO ligands and the two chlorides are related by the *C*₂ axis. This symmetry results in a planar four-membered InO_2Li ring in which the In and Li atoms are bridged by oxygen atoms. The bridging oxygens and nitrogen donor atoms constitute the equatorial component of an octahedral coordination geometry

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for (3)

Bond Lengths			
In(1)—Cl(1)	2.479(2)	N(2)—C(10)	1.465(10)
In(1)—N(3)	2.360(7)	N(3)—C(13)	1.491(10)
In(1)—Li	3.047(12)	O(1)—C(1)	1.322(10)
In(1)—O(1)	2.136(4)	C(6)—C(10)	1.504(11)
Li—N(2)	2.182(10)	C(2)—C(13)	1.522(11)
Li—O(1)	1.921(10)		
Bond Angles			
Cl(1)—In(1)—Li	90.3(1)	N(2)—Li—O(1)	92.3(2)
Cl(1)—In(1)—N(3)	92.6(2)	N(2)—Li—N(2A)	107.3(6)
Cl(1)—In(1)—O(1)	88.6(1)	O(1)—Li—O(1A)	88.1(6)
N(3)—In(1)—O(1)	88.0(2)	In(1)—N(3)—C(13)	105.0(4)
Cl(1)—In(1)—Cl(1A)	179.5(1)	Li—N(2)—C(10)	104.0(5)
N(3)—In(1)—N(3A)	107.0(3)	O(1)—Li—N(2A)	144.3(2)
O(1)—In(1)—O(1A)	77.4(3)		

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$) for 3

	x	y	z	$U(\text{eq})^a$
In(1)	115(1)	2500	54(1)	
Cl(1)	1681(1)	107(1)	2896(1)	77(1)
Li	2155(8)	2500	50(5)	
N(1)	3316(6)	772(6)	370(4)	101(4)
N(2)	1014(4)	3021(3)	2210(3)	67(2)
N(3)	113(4)	-826(4)	1660(3)	67(2)
O(1)	173(3)	1231(3)	1930(2)	55(2)
C(1)	717(5)	1171(4)	1527(3)	56(3)
C(2)	591(5)	486(5)	1080(3)	59(3)
C(3)	1140(6)	463(5)	639(4)	72(3)
C(4)	1801(6)	1096(5)	619(4)	71(3)
C(5)	1951(5)	1741(5)	1087(4)	71(3)
C(6)	1445(5)	1780(4)	1548(4)	62(3)
C(7)	2399(6)	1062(6)	139(4)	79(3)
C(8)	3868(9)	907(10)	-78(6)	145(7)
C(9)	3341(9)	-135(7)	573(6)	115(5)
C(10)	1719(5)	2400(5)	2091(4)	73(3)
C(11)	715(8)	3591(6)	1665(5)	100(4)
C(12)	1382(7)	3611(6)	2726(5)	97(4)
C(13)	-118(6)	-240(5)	1102(4)	68(3)
C(14)	1035(6)	-1234(5)	1698(5)	84(4)
C(15)	-553(6)	-1557(5)	1585(4)	86(4)
C(16)	380(22)	6092(8)	1952(12)	168(12)
C(17)	947(8)	6102(8)	2539(16)	193(14)
C(18)	562(15)	6107(8)	3065(10)	137(8)
C(19)	979(21)	6132(17)	1701(21)	158(19)
C(20)	8092(13)	2402(26)	35(12)	181(19)
C(21)	8440(22)	2000(15)	605(12)	209(19)
C(22)	7508(20)	2199(11)	436(8)	263(17)
C(23)	9030(14)	2237(24)	215(19)	388(28)
C(24)	6573(18)	2383(21)	261(14)	208(29)

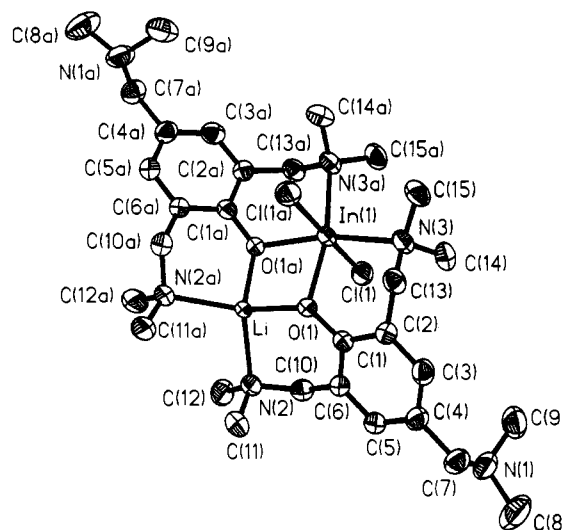
^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

around In(1). The bond angles for these atoms show significant deviations from the ideal octahedral values due to constraints imposed by the ligand (O(1)—In(1)—O(1A), 77.4(3)°; N(3)—In(1)—N(3A), 107.0(3)°; O(1)—In(1)—N(3), 88.0(2)°). The chloride ligands, however, adopt a near ideal axial Cl(1)—In(1)—Cl(1A) bond angle of 179.5(1)°. The In—O bond length (In(1)—O(1), 2.136(4) Å) may be compared with those in the neutral indium aryloxide complexes [In(μ -OR)]₂ (2.320 Å, $R_f = 2,4,6$ -(CF₃)₃C₆H₂)¹⁶ InCl(O₂C₆Cl₄)(C₆H₇N)₃ (average 2.128(7) Å),¹⁷ [In₂(dbc)₄(NH₃)₂]²⁻ (average 2.152(6) Å, dbc = 3,5-di-*tert*-butylcatecholate),¹⁸ and [Me₂In(OC₆H₄CHO)]₂ (average 2.285(3) Å).¹⁹ Neutral molecules with In₂O₂ cores include [*t*-Bu₂InOEt]₂ (average = 2.156(9) Å)²⁰ and [*t*-Bu₂In(OO-*t*-Bu)]₂

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**Figure 1.** Structure of 3 in the crystal showing the atom numbering chart. The hydrogen atoms are omitted for clarity.

(2.191(2) Å).²¹ Additionally, the In(1)—N(3) bond distance (2.360(7) Å) is similar to that in the neutral adduct Me₃In·NH₂-(*t*-Bu) (2.363(8) Å).²² This tendency for the group 13—group 15 bond length to remain relatively unchanged in anionic, as compared to neutral complexes, has been demonstrated previously for amidogallates²³ and perphosphido- and perarsenidogallates and indates.²⁴ Of related interest is the complex, Na[InL](NO₃)(H₂O)·C₂H₅OH (where L = tris(2'-(hydroxybenzyl)amino)ethyl)amine) in which there is a four-membered NaO₂In ring system.^{25,26} The average In—O bond distance in this complex is 2.168(4) Å (average).²¹

A combination of factors such as bridging heteroatom type and steric bulk appears to dictate the coordination environment for the Li⁺ counterion in group 13 anions. Thus, in complexes of the general formula M(EPh₂)₄Li(THF)₄, (M/E = Ga/P, In/P, and Ga/As) where the potential bridging group is P or heavier atom, the Li cation is separated from the anion and coordinated by four molecules of base.²⁴ In cases such as [(C₆H₁₁)₂Ga(NH(*t*-Bu)₂)Li(THF)₂],²³ the Li atom is incorporated into the Ga—N—Li—N four-membered ring. This is also the case when the bridging groups are oxygen, as in *e.g.* [Al(OCET₃)₃Cl]Li(THF)₂.²⁷ When bulky ligands are present around the group 13 metal, as in [AlMe(BHT)₂OC(Me)Ph₂]Li(Et₂O) (BHT = 2,6-(*t*-Bu)₂-4-(Me)C₆H₄O) the Li atom is still incorporated into the ring system, but with a lower coordination number (3).²⁸ Compound 3 is the culmination of this trend toward fewer supporting solvent groups, utilizing intramolecular base-

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stabilization to form a solvent free anion/cation pair. The geometry of the lithium atom in this complex is distorted square planar with bond angles of $88.1(6)^\circ$ (O(1)–Li–O(1A)), $107.3(6)^\circ$ (N(2)–Li–N(2A)), $92.3(2)^\circ$ (N(2)–Li–O(1)), and $144.3(2)^\circ$ (O(1)–Li–N(2A)). Interestingly, the ArⁿO ligand supports geometries around the Li and In where both atoms share the same equatorial plane. This is a rare example of a structurally characterized group 13 complex with an intramolecularly stabilized cation. On the basis of the similarities of the spectral features of **2** and **3**, an analogous solid-state structure can be postulated for **2**.

Finally, we note that, as expected, the *para* amine group does not participate in the bonding. However, this group is very useful as an internal NMR standard for determining the relative bonding environments of the *ortho* amine groups.

Conclusions

We have expanded the chemistry of the chelating aryloxide ligands to include group 13 examples of the bis-*ortho*-chelating ligand, 2,4,6-tris((dimethylamino)methyl)phenol. In principle, the synthetic strategy used for **1** can be employed for the preparation of a wide range of other metal halide derivatives.

An interesting facet of the present work concerns the intramolecular stabilization of the counteranion. Without problems of solvent loss, and consequent change in stoichiometry associated with traditional solvated anions, anions like **2** and **3** can potentially be used as well-behaved reagents in further syntheses. For instance, the anions could be used for salt elimination reactions with transition metal halides to form binuclear mixed-metal complexes. Current efforts are addressing this possibility.

Experimental Section

General Data. All compounds were prepared using standard vacuum line and drybox techniques. Toluene, benzene, and diethyl ether were distilled from sodium/benzophenoneketyl immediately prior to use. NMR spectra (¹H, ¹³C, and ³¹P) were recorded on a General Electric QE 300 spectrometer. All spectra were recorded in deuterated benzene at 25 °C and are referenced to Me₄Si. Mass spectral data were recorded on a Bell and Howell CEC 24-491 instrument for EI and a 70 eV MS, Finnigan MAT 4023 instrument for CI. The starting material, 2,4,6-tris((dimethylamino)methyl)phenol (ArⁿOH) was purchased from Aldrich and used as received. *n*-Butyllithium (Aldrich) was filtered and titrated immediately prior to use. The metallated complex ArⁿOLi was prepared by lithiation of ArⁿOH with *n*-BuLi in hexane. The resulting white microcrystalline solid was washed with hexane, dried under vacuum (10⁻³ Torr), and handled in the drybox.

Synthesis of (2,4,6-Tris((dimethylamino)methyl)phenoxy)dichlorogallane, [ArⁿOGaCl₂]₂ (1**).** To 1 equiv of ArⁿOLi (4.00 mmol, 1.085 g) in 50 mL of toluene was added a stirred solution of GaCl₃ (4.00 mmol, 0.704 g) in 20 mL of toluene at –78 °C. The reaction mixture was allowed to warm to 25 °C and then stirred (4 h) prior to filtration. The filtrate was evacuated (10⁻³ Torr) resulting in a clear glassy solid (yield 1.215 g, 75%). Mp: 120–122 °C rev; 175 dec. ¹H NMR (300.17 MHz) δ 2.16 (6H, s) *p*-NMe₂, 2.19 (12H, s) *o*-NMe₂, 3.40 (6H, s) CH₂NMe₂, 6.82 (2H, s) Ph-*H*. HRMS (CI, Neg): calcd, 806.14178; found, 806.140951. MS (CI, neg): 440 [ArⁿOGaCl₃]⁻. Anal. Calcd: C, 44.48; H, 6.47; N, 10.37. Found: C, 44.36; H, 6.51; N, 10.25.

Synthesis of Lithium [Bis(2,4,6-tris((dimethylamino)methyl)phenoxy)dichlorogallate], Li[(ArⁿO)₂GaCl₂] (2**).** Two equivalents of ArⁿOLi (8.00 mmol, 2.18 g) in 60 mL of toluene were added to a stirred solution of GaCl₃ (4.00 mmol, 0.70 g) in 20 mL of toluene at –78 °C. The reaction mixture was allowed to stir for 6 h prior to filtration. Solvent removal from the filtrate afforded 2.20 g of a white solid **2** (82% yield). Mp: 188–190 °C dec. ¹H NMR (300.17 MHz): δ 2.17 (12H, s) *p*-NMe₂, 2.20 (24H, s) *o*-NMe₂, 3.37 (8H, s) *o*-CH₂, 3.49 (4H, m) *p*-CH₂, 6.82 (4H, s) Ph-*H*. MS (CI, neg): 667, [(ArⁿO)₂GaCl₂]⁻. Anal. Calcd: C, 53.28; H, 7.75; N, 12.43. Found: C, 52.89; H, 7.68; N, 12.50.

Synthesis of Lithium [Bis(2,4,6-tris((dimethylamino)methyl)phenoxy)dichloroindate], Li[(ArⁿO)₂InCl₂] (3**).** Two equivalents of ArⁿOLi (8.00 mmol, 2.18 g) in 60 mL of toluene were added to a stirred solution of InCl₃ (4.00 mmol, 0.89 g) in 20 mL of toluene at –78 °C. The reaction mixture was allowed to stir for 6 h prior to filtration. Solvent removed from the filtrate afforded 2.45 g of white solid **3** (85% yield). Mp 91–93 °C rev. ¹H NMR (300.17 MHz): δ 2.17 (12H, s) *p*-NMe₂, 2.20 (24H, s) *o*-NMe₂, 3.36 (8H, s) *o*-CH₂, 3.45 (4H, m) *p*-CH₂, 6.83 (4H, s) Ph-*H*. MS (CI, neg): 720 M⁻; 678, M⁻ – LiCl. HRMS (CI, neg): calcd, 679.295728; found, 679.294038. Anal. Calcd: C, 49.95; H, 7.27; N, 11.65. Found: C, 50.21; H, 7.29; N, 11.52.

X-ray Experimental Data. Colorless, cubic (0.6 × 0.7 × 0.6 mm) crystals of **3** were sealed in a glass capillary (0.7 mm) and mounted on a Siemens R3m/v diffractometer. The final lattice parameters were determined from 25 accurately centered reflections ($2\theta > 30^\circ$) using Mo K α radiation (0.710 69 Å). During the data collection, the intensities of three monitored reflections decreased by <2%, and hence no correction was applied. The positions of the indium and chlorine atoms were determined from a Patterson map. Subsequent difference Fourier maps permitted the location of all non-hydrogen atoms. Difference peaks for the two disordered toluene molecules were symmetrically modeled by using the appropriate occupancy factors. All hydrogen atoms were placed in calculated positions and allowed to "ride" upon the appropriate carbon or nitrogen atoms. The largest parameter shifts in the final cycles of refinement were less than 0.01 of their estimated standard deviations. Neutral atom scattering factors were taken from the usual sources.²⁹ The structure was solved using the Siemens SHELXTL-PC software package. Refinement converged at $R = 0.0575$ and $R_w = 0.0772$ for 2358 reflections having $F > 4\sigma(F)$ using the weighting chart, $w = [(\sigma F)^2 + 0.0008F^2]^{-1}$. The largest parameter shifts in the final cycles of refinement were less than 0.01 of their estimated standard deviations.

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Supplementary Material Available: Tables giving crystallographic data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates and figures showing the complete molecular structure and a unit cell view for **3** (10 pages). Ordering information is given on any current masthead page.

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(29) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.