Synthesis, Structure, and Reactivity of a 2,3-Dialuminated Indole Derivative

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1-Methylindole was dimercurated upon treatment with mercuric acetate (2 equiv) in 1:1 ethanol−diethyl ether to afford 2,3-bis(acetoxymercurio)-1-methylindole (88%). 2,3-Bis(acetoxymercurio)-1-methylindole was converted to 2,3-bis(chloromercurio)-1-methylindole (92%) by refluxing with excess lithium chloride in methanol for 48 h. Treatment of 2,3-bis(chloromercurio)-1-methylindole with trimethylaluminum (4 equiv) in hexane afforded dimeric 2-(chloromethylaluminio)-3-(dimethylaluminio)-1-methylindole in 93% yield. The structure of dimeric 2-(chloromethylaluminio)-3-(dimethylaluminio)-1-methylindole was established by NMR, IR, and microanalysis and by an X-ray structure determination. Dimeric 2-(chloromethylaluminio)-3-(dimethylaluminio)-1-methylindole shows hindered rotation of the dimethylaluminio groups, with a barrier to rotation of 14.2 ± 0.2 kcal/mol. The molecular structure of dimeric 2-(chloromethylaluminio)-3-(dimethylaluminio)-1-methylindole was determined by X-ray crystallography and consists of a 2,3-dialuminated indole connected by a C_4Al_2 ring in a chair conformation. The C_4Al_2 ring is composed of two chloromethylaluminio groups bridging between the 2-position of one indole fragment and the 3-position of another. A dimethylaluminio group is bonded to the carbon at the 3-position in each indole ring, and a bridging chloride is situated between the dimethylaluminio and chloromethylaluminio units in each half of the dimeric structure.

Introduction

Organic aromatic compounds in which the aromatic hydrogens have been replaced by main-group metal substituents represent a rare class of molecules.[1] Recently, we have reported that ruthenocenes bearing pentalithiated,[2] pentamagnesiated,[3] and pentazincated[4] cyclopentadienyl ligands can be prepared by treatment of permercurated ruthenocenes[5] with the appropriate main-group metal alkyl. Successful preparation of permetalated ruthenocenes suggested that many permetalated organic aromatic compounds should be similarly accessible by transmetalation reactions starting from permercurated organic aromatic compounds.[6,7] As a prelude, we have begun exploring approaches to 2,3-dimetalated indoles[8,9] as models for more heavily metalated benzene derivatives. Gribble reported the preparation of several 2,3-dilithioindole derivatives,[8] but these compounds undergo rapid ring-opening reactions, even at −90 °C. Evidence for an intact 2,3-dilithioindole species was only obtained by observation of an 18% yield of 1-(phenylsulfonyl)indole upon treatment of 2,3-diiodo-1-(phenylsulfonyl)indole with *tert*-butyllithium at −90 °C, followed by hydrolysis. Herein we report the dimercuration of 1-methylindole, conversion of the dimercurated indole to a 2,3-dialuminated 1-methylindole, and a crystal structure of a 2,3-dialuminated 1-methylindole, as well as the reactivity of the 2,3-dialuminated 1-methylindole. In contrast to 2,3-dilithiated indole derivatives, the dialuminated indole described herein is stable at ambient and elevated temperatures and shows no tendency to undergo ring opening. The dialuminated indole is a rare example of a crystallographically characterized polyaluminated aromatic compound.

Results

The preparative chemistry is outlined in Scheme 1. Reaction of 1-methylindole (**1**) with mercuric acetate (2 equiv) in 1:1 ethanol−diethyl ether at 23 °C for 8 h afforded 2,3-bis(acetoxymercurio)-1-methylindole (**2**; 88%)

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[1] For leading references, see: Winter, C. H.; Seneviratne, K. N.; Bretschneider-Hurley, A. *Comments Inorg. Chem.* **1996**, *19*, 1. See also: Morton, M. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1995**, *117*, 7005. Rot, N.; Bickelhaupt, F. *Organometallics* **1997**, *16*, 5027.

[2] Bretschneider-Hurley, A.; Winter, C. H. *J. Am. Chem. Soc.* **1994**, *116*, 6468.

[3] Seneviratne, K. N.; Bretschneider-Hurley, A.; Winter, C. H. *J. Am. Chem. Soc.* **1996**, *118*, 5506.

[4] Seneviratne, K. N.; Winter, C. H. *Organometallics* **1997**, *16*, 2498.

[5] Han, Y.-H.; Heeg, M. J.; Winter, C. H. *Organometallics* **1994**, *13*, 3009. Winter, C. H.; Han, Y.-H.; Ostrander, R. L.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1161. Winter, C. H.; Han, Y.-H.; Heeg, M. J. *Organometallics* **1992**, *11*, 3169.

[6] For leading references, see: Deacon, G. B.; Farquharson, G. J. *Aust. J. Chem.* **1976**, *29*, 627. *J. Organomet. Chem.* **1974**, *67*, C1. O'Connor, G. N.; Crawford, J. V.; Wang, C.-H. *J. Org. Chem.* **1965**, *30*, 4090. Ciusa, R.; Grilla, G. *Gazz. Chim. Ital.* **1927**, *57*, 323. Paolini, O.; Silbermann, B. *Gazz. Chim. Ital.* **1915**, *45*, 385.

[7] For a feasibility study involving the preparation of a 1,4-dimagnesiated benzene derivative, see: Reck, C. E.; Winter, C. H. *Organometallics* **1997**, *16*, 4493.

[8] Gribble, G. W.; Saulnier, M. G. *J. Org. Chem.* **1983**, *48*, 607. See also: Gribble, G. W. *Synlett* **1991**, 289.

[9] For claims of polylithiated benzofuran, benzothiophene, and thiophene, see: Sévricourt, M. C.; Robba, M. *Bull. Soc. Chim. Fr.* **1977**, 142. Ried, W.; Bender, H. *Chem. Ber.* **1956**, *89*, 1574. Janda, M.; Srogl, J.; Stibor, I.; Nemec, M.; Vopatrna, P. *Synthesis* **1972**, 545.

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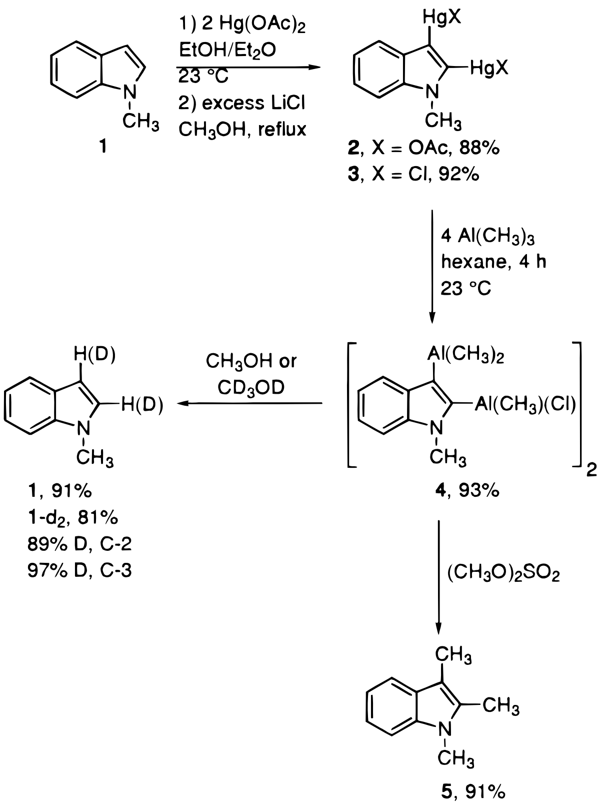
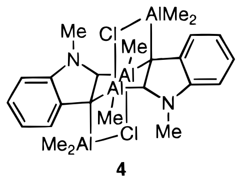
Scheme 1. Preparation and Reactions of 4



as a white powder. Compound **2** was converted to 2,3-bis(chloromercurio)-1-methylindole (**3**; 92%) by refluxing with excess lithium chloride in methanol for 48 h.

Treatment of **3** with trimethylaluminum (4 equiv) in hexane led to the dissolution of **3** within 10 min to afford a clear, colorless solution. Over 4 h, a white precipitate formed. Isolation of the white solid by decanting the reaction solution and vacuum-drying afforded the dialuminated indole **4** in 93% yield. The structure of **4** was established by NMR, IR, and microanalysis and by an X-ray structure determination. Despite many attempts, it was not possible to obtain microanalytical results that were consistently within ±0.4% of theory. However, the ^{1}H and ^{13}C{^{1}H} NMR spectra of purified material did not show any resonances beyond those expected for **4**, indicating a single, pure compound. Furthermore, the variable-temperature NMR behavior described below is entirely consistent with the proposed structure.



4

The ^{1}H NMR spectrum of **4** in toluene-d_8 at 23 °C showed three equal-intensity aluminum methyl resonances at δ 0.14, −0.20, and −1.27. The signal at δ 0.14 was a sharp singlet, while the resonances at δ −0.20 and −1.27 were broad singlets with peak widths of about 80 Hz at half-height. Collection of the ^{13}C{^{1}H} NMR spectrum of **4** at ambient temperature did not lead to the observation of the aluminum methyl groups, even with extended data collection. However, at −80 °C in toluene-d_8, the aluminum methyls were observed as sharp singlets at −4.71, −7.78, and −9.20 ppm. The ^{1}H NMR spectrum of **4** in toluene-d_8 at −80 °C showed sharp singlets for the aluminum methyl groups at δ 0.27, 0.08, and −1.11. Upon warming to 20 °C, the two highest field resonances gradually became broader (Figure 1). As the temperature increased, the peaks at δ 0.08 and −1.11 gradually coalesced into a single peak. The coalescence temperature was found to be 46.0 °C. At 70 °C, two resonances were observed for the aluminum-bound methyls, one at δ 0.11 and the other at δ −0.79. These two peaks were integrated in a 1:2 ratio, respectively. The dynamic process was completely reversible; *i.e.*, cooling from 70 °C to 20 °C led to decoalescence to afford three aluminum methyl resonances at δ 0.14, −0.20, and −1.27. Considering the variable-temperature behavior, we assign the resonance at δ 0.14 to the methyl group of the chloromethylaluminio group and the resonances at δ −0.20 and −1.27 to the dimethylaluminio group. A free energy of activation ($\Delta G^{\ddagger}$) of 14.2 ± 0.2 kcal/mol can be calculated from the ^{1}H NMR data.[10]

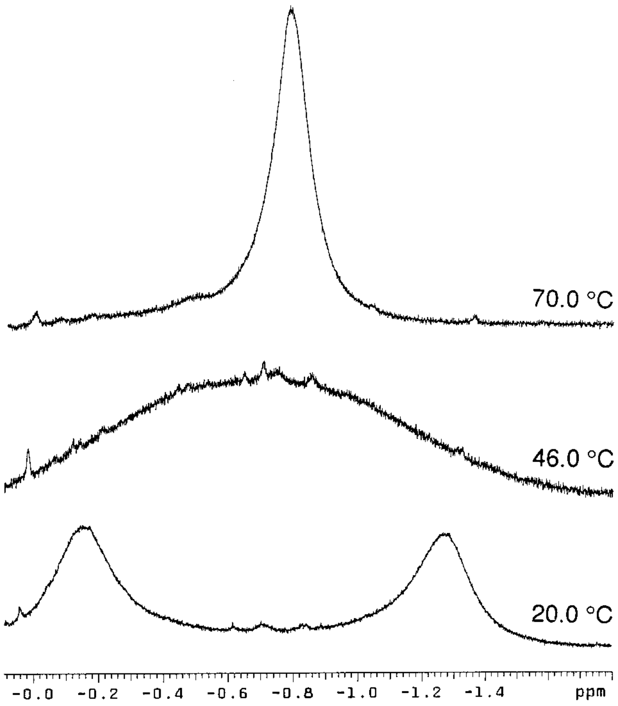


Figure 1. Expansion of the dimethylaluminio resonance region in the variable-temperature ^{1}H NMR spectra of **4**.

The reactivity of **4** is outlined in Scheme 1. These reactions were initially probed under conditions where **4** was generated in solution, as described in the Experimental Section. Hydrolysis with methanol afforded 1-methylindole in 91% yield, while deuteriolysis with methanol-d_4 afforded 1-methylindole-d_2 in 81% yield with 89 and 97% deuterium incorporation at the 2- and 3-positions, respectively. Methylation with dimethyl sulfate afforded 1,2,3-trimethylindole in 91% yield. Reactions were also performed with **4** that had been isolated and purified. The yields were nearly identical (±5%) with those described above, where **4** was gener-

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(10) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; pp 96−97.

Table 1. Experimental Crystallographic Data for 4

empirical formula	$C_{24}H_{32}Al_4Cl_2N_2$	V (Å^3)	728.78(13)
fw	527.34	Z	1
space group	$P\bar{1}$	T (K)	295(2)
a (Å)	8.5366(8)	λ (Å)	0.710 73
b (Å)	10.0106(9)	ρ(calcd) (g cm^{-3})	1.202
c (Å)	10.3984(13)	μ (mm^{-1})	0.358
α (deg)	64.294(2)	$R(F)$ (%)	6.4
β (deg)	65.768(2)	$R_w(F)$ (%)	11.8
γ (deg)	82.626(2)		

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

Al(1)−C(10)	1.940(3)	C(2)−C(3)	1.466(3)
Al(1)−C(1)	2.001(2)	C(3)−C(4)	1.400(3)
Al(1)−C(2)#1	2.009(2)	C(3)−C(8)	1.405(3)
Al(1)−Cl(1)	2.3163(9)	C(4)−C(5)	1.389(4)
Al(2)−Cl(1)	2.3484(10)	C(4)−N(1)	1.395(3)
Al(2)−C(11)	1.955(3)	N(1)−C(9)	1.466(3)
Al(2)−C(12)	1.944(4)	C(5)−C(6)	1.373(4)
Al(2)−C(2)	2.065(2)	C(6)−C(7)	1.378(5)
C(1)−N(1)	1.347(3)	C(7)−C(8)	1.365(4)
C(1)−C(2)	1.431(3)		
C(10)−Al(1)−C(1)	123.10(14)	C(12)−Al(2)−Cl(1)	104.5(2)
C(10)−Al(1)−C(2)#1	119.4(2)	C(11)−Al(2)−Cl(1)	104.2(2)
C(1)−Al(1)−C(2)#1	106.83(9)	C(2)−Al(2)−Cl(1)	98.96(7)
C(10)−Al(1)−Cl(1)	107.75(13)	N(1)−C(1)−Al(1)	131.2(2)
C(1)−Al(1)−Cl(1)	93.78(7)	C(2)−C(1)−Al(1)	119.8(2)
C(2)#1−Al(1)−Cl(1)	100.22(7)	C(1)−C(2)−Al(1)#1	110.6(2)
Al(1)−Cl(1)−Al(2)	96.95(3)	C(3)−C(2)−Al(1)#1	116.7(2)
C(12)−Al(2)−C(11)	120.9(2)	C(1)−C(2)−Al(2)	104.4(2)
C(12)−Al(2)−C(2)	108.9(2)	C(3)−C(2)−Al(2)	112.2(2)
C(11)−Al(2)−C(2)	116.2(2)	Al(1)#1−C(2)−Al(2)	107.41(10)

ated in solution. Other electrophiles that were allowed to react with **4** include allyl bromide, acetone, phenylacetyl chloride, benzophenone, phenyl iodide (under Pd(0) catalysis), phenylacetylene (under Pd(II) catalysis), acetyl chloride (under Pd(0) catalysis), dimethyl oxalate, and carbon dioxide. After aqueous workup, the crude reaction mixtures gave primarily **1** and, in several cases, ≤10% yields of monosubstituted products. These reactions were not pursued further. Several attempts were made to break up the dimeric structure of **4** by addition of Lewis bases that would coordinate to the aluminum centers. Treatment of **4** with tetrahydrofuran (2−3 equiv per aluminum center) in toluene afforded a totally insoluble product that could not be characterized further. Analysis by ^{1}H NMR in toluene-d_8 of the product obtained by treatment of **4** with pyridine (2 equiv per aluminum center) showed the presence of **4** and uncoordinated pyridine. Therefore, an equilibrium between **4** and pyridine to form an adduct with aluminum−pyridine bonds, if present at all, must strongly favor **4** and free pyridine at 23 °C.

The X-ray crystal structure of **4** was determined to establish its molecular geometry. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Table 2, and a perspective view is presented in Figure 2. The molecule is a dimeric 2,3-dialuminated indole connected by a C_4Al_2 ring in a chair conformation. The C_4Al_2 ring is composed of two chloromethylaluminio groups bridging between the 2-position of one indole fragment and the 3-position of another. A dimethylaluminio group is bonded to the carbon at the 3-position in each indole ring, and a bridging chloride is situated between the dimethylaluminio and chloromethylaluminio units in each half of the dimeric structure. An inversion center is present in the molecule. The groups bonded to Al(1) include the terminal methyl group (Al(1)−C(10) = 1.940(3) Å), the indole carbons (Al(1)−C(1) = 2.001(2) Å, Al(1)−C(2)# = 2.009(2) Å), and the chlorine atom (Al(1)−Cl(1) = 2.3163(9) Å). The bond lengths of Al(1) to the indole carbons are identical within experimental error and are slightly longer than that of the terminal methyl group. The bond length to the chlorine atom is typical for chlorines bridging between two aluminum atoms.[11,12] The groups bonded to Al(2) include two methyl groups (Al(2)−C(11) = 1.955(3) Å, Al(2)−C(12) = 1.944(4) Å), an indole carbon (Al(2)−C(2) = 2.065(2) Å), and the chlorine atom (Al(2)−Cl(1) = 2.3484(10) Å). Interestingly, the Al(2)−C(2) bond length is about 0.06 Å longer than the related values for Al(1)−C(1) and Al(1)−C(2)#1. The chloromethylaluminio group is more electrophilic than a dimethylaluminio group, and this may account for the difference in aluminum−carbon bond lengths between the two sites. The more electrophilic nature of the chloromethylaluminio group, compared to the dimethylaluminio unit, may also account for its bridging between the indole fragments. The bond lengths associated with the indole five-membered ring (C(1)−C(2) = 1.431(3) Å, C(2)−C(3) = 1.466(3) Å, C(3)−C(4) = 1.400(3) Å, C(4)−N(1) = 1.395(3) Å, C(1)−N(1) = 1.347(3) Å) are normal for indole systems, except that the C(1)−N(1) bond length is approximately 0.05 Å shorter than the value for C(4)−N(1).

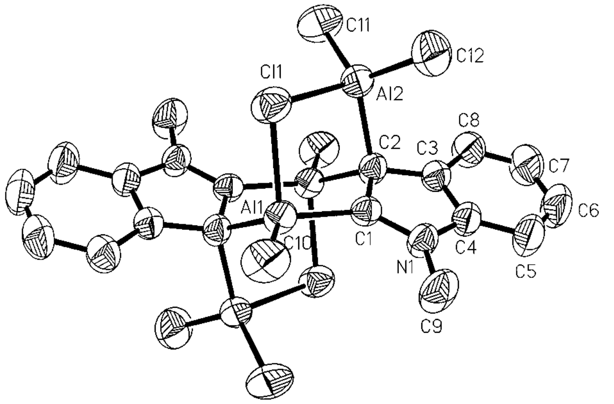

Figure 2. Perspective view of **4** with thermal ellipsoids at the 50% probability level.

Discussion

The most significant aspect of this work is the structure and characterization of the dialuminated indole **4**. Polyaluminated organic aromatic compounds are extremely rare, and accordingly, little is known about their properties. The only other dialuminated aromatic compound that has been structurally charac-

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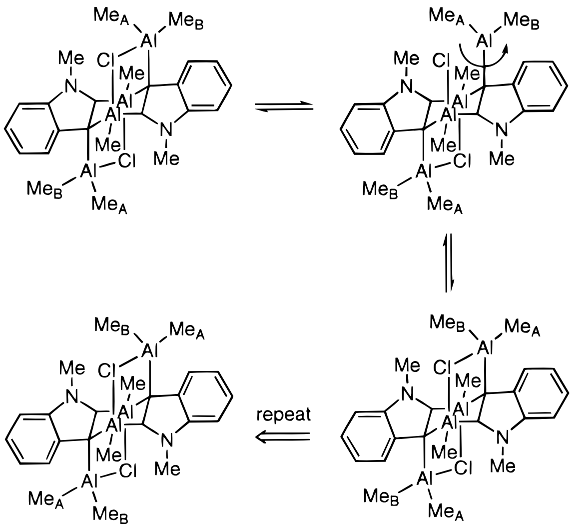
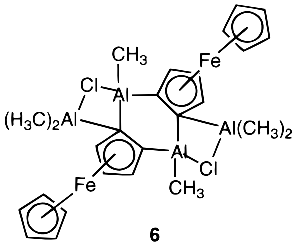
(11) For selected X-ray crystal structures of aluminum compounds with bridging chlorides, see: Wehmschulte, R. J.; Grigsby, W. J.; Schiemenz, B.; Bartlett, R. A.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 6694. Schulz, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Organomet. Chem.* **1995**, *493*, 69. Lalama, M. S.; Kampf, J.; Dick, D. G.; Oliver, J. P. *Organometallics* **1995**, *14*, 495. Hausen, H.-D.; Todtmann, J.; Weidlein, J. *J. Organomet. Chem.* **1994**, *466*, C1.

(12) Atwood, J. L.; Shoemaker, A. L. *J. Chem. Soc., Chem. Commun.* **1976**, 536. See also: Atwood, J. L.; Bailey, B. L.; Kindberg, B. L.; Cook, W. J. *Aust. J. Chem.* **1973**, *26*, 2297. Rogers, R. D.; Cook, W. J.; Atwood, J. L. *Inorg. Chem.* **1978**, *18*, 279.

Scheme 2. Rotational Process



terized is the 1,2-dialuminated ferrocene $[(C_5H_5)Fe(C_5H_3)Al_2(CH_3)_3Cl]_2$ (**6**).[12] Complex **6** was prepared in low yield as a byproduct of the reaction of 1,1′-bis(chloromercurio)ferrocene with trimethylaluminum. Like **6**, **4** forms with one dimethylaluminio group and one chloromethylaluminio group per indole moiety, exists in a dimeric structure, and crystallizes with the C_4Al_2 ring in a chair conformation. However, the rings that contain the bridging chlorides in **4** are five-membered rings, while the analogous rings in **6** are four-membered cycles. The difference between **4** and **6** is that the chlorines adopt axial positions in **4**, while they adopt equatorial positions in **6**. The chlorine atom stereochemistry therefore dictates whether the 5−6−5 or 4−6−4 ring system is obtained. In order for **4** to crystallize in a 4−6−4 ring system, an aluminum−carbon bond would have to break to allow rotation of the chloromethylaluminio substituent. We did not observe any evidence for such a process but cannot rule it out. It is possible that the 5−6−5 ring system present in **4** and the 4−6−4 ring system present in **6** are similar in energy, and the choice between these systems may be determined by crystal-packing forces and the tendency of the particular conformation to crystallize efficiently.



6

Complex **4** exhibits a dynamic process in the ^{1}H NMR spectra that affects only the dimethylaluminio groups. The observed behavior is consistent with a simple two-site exchange process. A process that fits the experimental observations is rate-determining cleavage of the Al(2)−Cl(1) bond, followed by rapid dimethylaluminio rotation and re-formation of the bridging chloride bond (Scheme 2). The rotational barrier for a $C-Al(CH_3)_2$ bond without a bridging chloride attached to the aluminum center must be very low. Accordingly, the observed barrier of 14.2 ± 0.2 kcal/mol must substantially reflect the energy associated with breaking the Al(2)−Cl(1) bond. Moreover, this value must correspond to the upper limit of the Al(2)−Cl(1) bond strength. Due to the limited solubility of **4** in toluene-d_8 (only a few milligrams dissolved at 23 °C), it was not possible to vary the concentration of **4** in a meaningful way to probe for intramolecular versus intermolecular exchange processes. Attempts to measure a molecular weight for **4** by freezing point depression techniques in benzene were unsuccessful, due to the precipitation of **4** in this solvent near the freezing point.

Some final comments can be made on the synthetic route that leads to **4**, which entails treatment of mercurated precursor **3** with trimethylaluminum. Reaction of mono- and dimercurated ferrocenes with trimethylaluminum has been documented as a route to ferrocenylalanes.[12] We have recently demonstrated that permetalated ruthenocenes[2−4] and a dimagnesiated benzene derivative[7] can be easily prepared by treatment of a mercurated precursor with the appropriate main-group-metal alkyl. The results of this study, coupled with our previous work, demonstrate that main-group-metal−mercury transmetalations constitute an efficient route to polymetalated organic aromatic compounds. Polymetalated aromatic compounds are not well-documented but are of theoretical interest and may have applications in synthesis. We are continuing to explore the synthesis, structure, and reactivity of heavily metalated organic aromatic compounds and will report our findings in due course.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of argon using either a Schlenk line with appropriate glassware or a glovebox. Hexane and toluene were distilled from sodium prior to use. Toluene-d_8 was distilled from sodium, while chloroform-*d* was dried over molecular sieves. DMSO-d_6 was used as received. 1-Methylindole, mercuric acetate, lithium chloride, trimethylaluminum (as a 2.0 M solution in hexane), and dimethyl sulfate were used as received from commercial sources. ^{1}H and ^{13}C{^{1}H} spectra were obtained at 500 and 121 MHz, respectively, in the indicated solvents. Infrared spectra used potassium bromide, Nujol, or Fluorolube as the matrixes, as indicated. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on an Electrothermal Model 9200 melting point apparatus and are uncorrected.

Caution! The synthetic procedures involve the generation of organomercury compounds. Reactions should be run in closed vessels in a fume hood, and extreme care should be exercised in dealing with the chemical waste that is generated.

Preparation of 2,3-Bis(acetoxymercurio)-1-methylindole (2). A 500-mL round-bottomed flask was charged with mercuric acetate (10.0 g, 31.4 mmol), 1-methylindole (2.00 mL, 15.7 mmol), diethyl ether (150 mL), and ethanol (150 mL). A white turbid solution resulted. The mixture was stirred for 8 h. The resulting white solid was collected on a medium-porosity glass frit and was washed successively with water (300 mL), ethanol (200 mL), and diethyl ether (100 mL). The solid was dried under vacuum at 65 °C for 12 h to afford **2** (8.96 g, 88%): dec range 240−250 °C; IR (KBr, cm^{-1}) 3098 (w), 3079 (w), 3049 (m), 3030 (w), 3016 (w), 2928 (s), 2830 (w), 1624 (s), 1593 (s), 1500 (m), 1460 (s), 1438 (s), 1407 (s), 1370 (s), 1313 (s), 1236 (m), 1228 (m), 1181 (w), 1156 (m), 1130 (m), 1106 (m), 1046 (m), 1028 (m), 1010 (m), 944 (w), 931 (w), 837 (w), 826 (w), 814 (w), 793 (w), 752 (m), 738 (s), 691 (s), 668 (m), 645 (w), 616 (w), 595 (w), 562 (w), 546 (w), 516 (w); ^{1}H NMR (DMSO-d_6, δ) 7.49 (d, J = 7.8 Hz, 4- or 7-$\boldsymbol{H}$), 7.38 (d, J = 7.8 Hz, 4- or 7-$\boldsymbol{H}$), 7.08 (m, 5- or 6-$\boldsymbol{H}$), 6.99 (m, 5- or 6-$\boldsymbol{H}$), 3.82 (s, N−C$\boldsymbol{H}_3$), 1.98 (s, 2 HgOCOC$\boldsymbol{H}_3$); ^{13}C{^{1}H} NMR (DMSO-d_6, ppm) 174.83 (2 HgO$\boldsymbol{C}$OCH$_3$), 138.05 (quaternary $\boldsymbol{C}$ at C-8), 133.02 ($\boldsymbol{C}$−Hg at C-2), 122.31 (quaternary $\boldsymbol{C}$ at C-9), 121.19 (indole $\boldsymbol{C}$−H at C-4 or C-6), 120.97 (indole $\boldsymbol{C}$−H at C-4 or C-6), 118.78 ($\boldsymbol{C}$−Hg at C-3), 118.54 (indole $\boldsymbol{C}$−H at C-5), 109.61 (indole $\boldsymbol{C}$−H at C-7), 34.99 (N−$\boldsymbol{C}$H$_3$), 23.41 (2 CO$_2\boldsymbol{C}$H$_3$). Anal. Calcd for $C_{13}H_{13}Hg_2NO_4$: C, 24.08; H, 2.02. Found: C, 24.87; H, 2.12.

Preparation of 2,3-Bis(chloromercurio)-1-methylindole (3). A 500-mL round-bottomed flask was charged with **2** (10.1 g, 15.6 mmol), lithium chloride (1.45 g, 34.3 mmol), methanol (300 mL), and a magnetic stirbar. The flask was equipped with a condenser, and the contents were refluxed for 2 days. Upon cooling, the resultant white solid was collected on a medium-porosity frit and was washed successively with water (300 mL), methanol (200 mL), and diethyl ether (200 mL). Vacuum drying at 65 °C for 16 h afforded **3** (8.63 g, 92%): dec range 260−270 °C; IR (KBr, cm^{-1}) 3045 (w), 3013 (w), 2929 (s), 2862 (w), 2831 (w), 1475 (m), 1461 (s), 1439 (s), 1408 (s), 1384 (m), 1344 (m), 1321 (s), 1300 (m), 1228 (s), 1190 (m), 1155 (m), 1130 (m), 1104 (m), 1010 (m), 940 (w), 928 (w), 848 (w), 791 (m), 748 (s), 612 (w), 595 (w), 544 (w), 437 (w); ^{1}H NMR (DMSO-d_6, δ) 7.53 (d, J = 8.1 Hz, 4- or 7-$\boldsymbol{H}$), 7.37 (d, J = 8.1 Hz, 4- or 7-$\boldsymbol{H}$), 7.07 (m, 5- or 6-$\boldsymbol{H}$), 6.97 (m, 5- or 6-$\boldsymbol{H}$), 3.81 (s, N−C$\boldsymbol{H}_3$); ^{13}C{^{1}H} NMR (DMSO-d_6, ppm) 137.68 (quaternary $\boldsymbol{C}$ at C-8), 132.70 ($\boldsymbol{C}$-Hg at C-2), 122.45 (quaternary $\boldsymbol{C}$ at C-9), 121.40 (indole $\boldsymbol{C}$−H at C-4 or C-6), 120.95 (indole $\boldsymbol{C}$−H at C-4 or C-6), 118.80 ($\boldsymbol{C}$−Hg at C-3), 118.62 (indole $\boldsymbol{C}$−H at C-5), 109.52 (indole $\boldsymbol{C}$−H at C-7), 35.07 (N−$\boldsymbol{C}$H$_3$). Anal. Calcd for $C_9H_7Cl_2Hg_2N$: C, 17.98; H, 1.17. Found: C, 18.13; H, 1.21.

Preparation of 4. A 100-mL Schlenk flask was charged with **3** (0.900 g, 1.50 mmol) and hexane (30 mL). A 2.0 M solution of trimethylaluminum in hexane (3.00 mL, 6.00 mmol) was added to the suspension. The solution was stirred for 4 h at ambient temperature to afford a white solid. The solution was decanted, and the white solid was washed with hexane (10 mL). The resultant solid was dried under vacuum at 65 °C for 12 h to afford **4** (0.368 g, 93%): dec range 162−182 °C; IR (Nujol, cm^{-1}) 1213 (m), 1200 (m), 1180 (m), 1131 (w), 1088 (w), 1015 (w), 934 (w), 922 (w), 789 (m), 755 (m), 745 (m), 687 (s), 667 (s), 650 (s); IR (Fluorolube, cm^{-1}) 3070 (w), 3036 (w), 3013 (w), 2928 (s), 2884 (s), 2818 (m), 1576 (m), 1569 (m), 1558 (s), 1540 (s), 1533 (m), 1521 (w), 1507 (s), 1497 (w), 1489 (w), 1473 (m); ^{1}H NMR (toluene-d_8, −80 °C, δ) 7.65 (d, J = 4.8 Hz, 4- or 7-$\boldsymbol{H}$), 7.20 (m, 5- or 6-$\boldsymbol{H}$), 7.14 (m, 5- or 6-$\boldsymbol{H}$), 6.84 (d, J = 4.8 Hz, 4- or 7-$\boldsymbol{H}$), 3.38 (s, NC$\boldsymbol{H}_3$), 0.26 (s, ClAlC$\boldsymbol{H}_3$), 0.08 (s, Al(C$\boldsymbol{H}_3$)(CH$_3'$)), −1.11 (s, Al(CH$_3$)(C$\boldsymbol{H}_3'$)); ^{13}C{^{1}H} NMR (toluene-d_8, −80 °C, ppm) 144.67 (indole $\boldsymbol{C}$−H), 144.40 ($\boldsymbol{C}$−Al at C-2 or quaternary carbon at C-8 or C-9), 141.70 ($\boldsymbol{C}$−Al at C-2 or quaternary carbon at C-8 or C-9), 142.34 (indole $\boldsymbol{C}$−H), 122.72 ($\boldsymbol{C}$−Al at C-3 or quaternary carbon at C-8 or C-9), 122.53 ($\boldsymbol{C}$−Al at C-3 or quaternary carbon at C-8 or C-9), 111.96 (indole $\boldsymbol{C}$−H), 94.76 (indole $\boldsymbol{C}$−H), 35.98 (N−$\boldsymbol{C}$H$_3$), −4.71 (Al(Cl)-($\boldsymbol{C}$H$_3$)), −7.78 (Al($\boldsymbol{C}$H$_3$)(CH$_3'$)), −9.20 (Al(CH$_3$)($\boldsymbol{C}$H$_3'$)). Anal. Calcd for $C_{24}H_{32}Al_4Cl_2N_2$: C, 54.66; H, 6.12; Cl, 13.45. Found: C, 53.53; H, 6.04; Cl, 12.64.

Treatment of 4 with Methanol. Compound **4** was generated as above from **3** (0.508 g, 0.845 mmol) and a 2.0 M solution of trimethylaluminum in hexane (1.70 mL, 3.38 mmol) in hexane (20 mL). Methanol (0.500 mL, 12.3 mmol) was added to the solution at room temperature, and the mixture was stirred for 1 h. The solvent was removed under reduced pressure, and the residue was extracted with dichloromethane (30 mL). The extract was passed through a 2-cm pad of silica gel on a coarse glass frit. Elution with dichloromethane (50 mL), followed by removal of the solvent under reduced pressure, afforded **1** (0.101 g, 91%) as a yellow liquid. The ^{1}H and ^{13}C{^{1}H} NMR spectra of this material were identical with those of pure **1**.

Treatment of 4 with Methanol-d_4. Compound **4** was generated as above from **3** (0.604 g, 1.00 mmol) and a 2.0 M solution of trimethylaluminum in hexane (2.00 mL, 4.00 mmol) in hexane (20 mL). Methanol-d_4 (0.500 mL, 12.3 mmol) was added to the solution at room temperature, and the solution was stirred for 1 h. The solvent was removed under reduced pressure, and the residue was extracted with dichloromethane (30 mL). The extract was passed through a 2-cm pad of silica gel on a coarse glass frit. Elution with dichloromethane (50 mL), followed by removal of the solvent under reduced pressure, afforded **1** (0.108 g, 81%) as a yellow liquid: ^{1}H NMR (CDCl$_3$, δ) 7.75 (d, J = 7.8 Hz, 4- or 7-$\boldsymbol{H}$), 7.41 (d, J = 7.8 Hz, 4- or 7-$\boldsymbol{H}$), 7.33 (m, 5- or 6-$\boldsymbol{H}$), 7.23 (m, 5- or 6-$\boldsymbol{H}$), 7.12 (s, C-2, 11% residual H), 6.60 (s, C-3, 3% residual H), 3.84 (s, NC$\boldsymbol{H}_3$).

Treatment of 4 with Dimethyl Sulfate. Compound **4** was generated as above from **3** (0.601 g, 1.00 mmol) and a 2.0 M solution of trimethylaluminum in hexane (2.00 mL, 4.00 mmol) in hexane (20 mL). Dimethyl sulfate (0.570 mL, 6.00 mmol) was added to the solution at room temperature. The solution was stirred for 4 h, at which point the reaction was quenched with methanol (1 mL). The solvent was removed under reduced pressure, and the residue was extracted with dichloromethane (30 mL). The extract was passed through a 2-cm pad of silica gel on a coarse glass frit. Elution with dichloromethane (50 mL), followed by removal of the solvent under reduced pressure, afforded a yellow liquid. Distillation using a Kugelrohr apparatus at 86−90 °C (0.01 Torr) afforded **5** (0.145 g, 91%) as a pale yellow liquid: ^{1}H NMR (CDCl$_3$, δ) 7.61 (d, J = 7.8 Hz, 4- or 7-$\boldsymbol{H}$), 7.28 (d, J = 7.8 Hz, 4- or 7-$\boldsymbol{H}$), 7.16 (m, 5- or 6-$\boldsymbol{H}$), 7.09 (m, 5- or 6-$\boldsymbol{H}$), 3.67 (s, NC$\boldsymbol{H}_3$), 2.38 (s, C$\boldsymbol{H}_3$ at C-2 or C-3), 2.37 (s, C$\boldsymbol{H}_3$ at C-2 or C-3); HRMS calcd for $C_{11}H_{13}N$ 159.104 79, found 159.104 65.

Calculation of Free Energy of Coalescence for 4. A 5-mm NMR tube was charged with **4** (0.012 g, 0.020 mmol) and toluene-d_8 (0.8 mL) and was fitted with a rubber septum. Only a portion of **4** dissolved at 23 °C (*ca.* 2−3 mg). The tube was transferred to the NMR probe, and the ^{1}H NMR spectra (500 MHz) were recorded between −80 and +70 °C. At −80 °C, the dimethylaluminio methyl resonances were observed at δ 0.08 and −1.11, with a separation ($\Delta\nu$) of 594 Hz. When the sample was warmed to 20 °C, the two resonances had become very broad. The two dimethylaluminio resonances coalesced into one peak at 46.0 °C. At 70.0 °C, the dimethylaluminio resonance was observed as a single peak at δ −0.77. Application of the standard dynamic NMR equation for an AB system[10] affords a barrier of 14.2 ± 0.2 kcal/mol for dimethylaluminio group rotation. The chloromethylaluminio methyl resonance remained a sharp singlet between −80 and +70 °C, and its chemical shift changed only slightly (−80 °C, δ 0.27; 20.0 °C, δ 0.16; 70.0 °C, δ 0.12).

Crystal Structure of 4. A crystal of **4** suitable for the diffraction experiment was grown from a hexane solution at −20 °C. The sample was mounted in a thin-walled capillary tube under a nitrogen atmosphere. Crystallographic data were collected at room temperature on a Siemens/Bruker automated P4/CCD diffractometer with monochromated Mo radiation. A total of 1360 frames were collected at 10 s and integrated with the SMART and SAINT software. Absorption corrections were applied with the SADABS program, and the structure was solved and refined using the programs of SHELXS-86 and SHELXL-93. Crystal data are presented in Table 1. Results are presented in Table 2 and Figure 2. Other data are available in the Supporting Information. Compound **4** crystallized as a discrete molecular complex with no associated solvents or ions. All atoms occupy general crystallographic positions, but the molecule lies on an inversion center. Hydrogen atoms were placed in observed positions and were refined. All non-hydrogen atoms were described anisotropically.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, bond distances and angles, and hydrogen coordinates for **4** (5 pages). Ordering information is given on any masthead page.

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