Synthesis and Characterization of a Trigallacycle

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The reaction of equimolar quantities of 1,8-bis(trimethylstannyl)naphthalene (**1**) and $GaCl_3$ in toluene at −25 °C yields the known stannagallacycle bis(μ-1,8-naphthalenediyl)(μ-chloride)-methyltin(IV)chlorogallium(III) (**2**) and a new product which has been identified as the cyclic adduct formed between two molecules of bis(μ-1,8-naphthalenediyl)bis(gallium(III)chloride) and two molecules of trimethyltin chloride (**3**). Interestingly, when carried out at 25 °C and in the presence of water, this reaction leads to the formation of an additional product (**4**) that is a 12-membered macrocycle containing three gallium atoms linked by 1,8-naphthalenediyl ligands and arranged about a central oxygen atom. The charge balance of **4** is achieved by the presence of a chloride atom that occupies a bridging position between two of the gallium centers. Compounds **3** and **4** have been characterized by NMR, elemental analysis, and single-crystal X-ray analysis. In the crystal, **4** exists as a dimer wherein the monomers are bridged via a Ga−O−Ga−O four-membered ring. The solution structure of **4** in THF-d_8 has been investigated by pulse field gradient spin−echo (PGSE) methods and VT ^{1}H NMR spectroscopy. The PGSE measurements suggest that, in solution, **4** undergoes a rapid monomer−dimer equilibrium. VT ^{1}H NMR spectroscopy confirms the existence of a fluxional system. The high-temperature spectrum exhibits three sharp signals. Upon cooling, each of the three sharp signals decoalesces into three signals. Simulation of the spectra followed by an Eyring analysis afforded $\Delta H^{\ddagger} = 43 \pm 3$ kJ·mol^{-1} and $\Delta S^{\ddagger} = -36 \pm 9$ J·K^{-1}·mol^{-1} for this process. As a whole, these results support the existence of an exchange between the monomeric and dimeric form of **4**. The high-temperature data suggest that upon dissociation into the monomer, the chloride anion undergoes rapid exchange leading to an apparent three-fold molecular symmetry.

Introduction

The chemistry of macrocyclic polydentate Lewis acids has matured into a multifaceted area of chemistry. In the field of molecular recognition, these species have proved useful for the selective complexation of anionic guests.[1−4] More recently, extension of their coordination chemistry to the case of neutral electron-rich guests[1,5] has found applications in the field of supramolecular catalysis[6] and crystal engineering.[7] While these achievements substantiate the fertility of the field, it is interesting to note that the vast majority of macrocyclic polydentate Lewis acids[8] contain relatively weak Lewis acidic elements such as tin[3,4] and mercury.[1,2,5−7] Motivated by the chemistry developed with small group 13 bidentate Lewis acids in the field of anion complexation,[9] molecular recognition,[10] and catalysis,[11] we have initiated an effort focused on the synthesis and coordination chemistry of macrocyclic species containing several group 13 elements. Herein, we wish to report on the preparation and properties of a trigallacycle.

Results and Discussions

Recently, we reported that the reaction of equimolar quantities of 1,8-bis(trimethylstannyl)naphthalene (**1**)[12]

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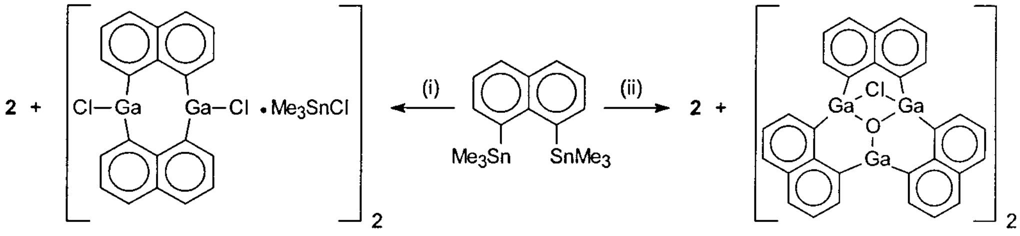
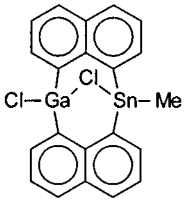
Scheme 1[a]



3 **1** **4**

[a] (i) GaCl$_3$, toluene, −25 °C; (ii) H$_2$O, GaCl$_3$, toluene, 25 °C

and GaCl$_3$ in toluene yields a stannagallacycle, namely, bis(*μ*-1,8-naphthalenediyl)(*μ*-chloride)methyltin(IV)-chlorogallium(III) (**2**) as a major product which was isolated in a 65% yield when the reaction was carried out at 65 °C.[13]



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Interestingly, when this reaction is carried out at −25 °C, the formation of a crystalline precipitate containing two types of morphologically distinguishable crystals is observed. Analysis of the different crystals indicates that the main product of the reaction is **2**, which is isolated as irregular shaped crystals in a 21% yield. The second type of crystal is clear, colorless as well as cubic and corresponds to a new product (**3**) which forms in a 10% yield (Scheme 1). Compound **3** has been characterized by ^{1}H, ^{13}C, and ^{119}Sn NMR, elemental analysis, and X-ray crystallography. This compound is an adduct formed between bis(*μ*-1,8-naphthalenediyl)bis-(gallium(III)chloride) and trimethyltin chloride. In the crystal, this adduct adopts a dimeric structure in which the monomers are linked via two pentacoordinated tin atoms (Table 1, Figure 1). The resulting macrocycle is centrosymmetric. The digallacycle units exhibit a folded structure with a dihedral angle between the naphthalene rings of 133.9°. Each gallium center features a distorted tetrahedral geometry. The deviations from an ideal geometry are especially manifest in the obtuse C−Ga−C angles (av 133.3°). The geometrical constraints present in the structure of **3** induce distortions of the naphthalenediyl fragments similar to those encountered in other hindered *peri*-substituted naphthalene systems.[14−16] Although **3** was isolated in low yield, its formation indicates that the exchange of both stannyl groups of **1** by gallium moieties is possible. Compound **3** dissolves only in polar solvents. Its NMR spectroscopic features have been studied in pyridine-*d*$_5$. While the ^{1}H and ^{13}C NMR spectrum reveals the presence of a symmetrically substituted naphthalene ring, the ^{119}Sn signal observed at −16 ppm corresponds to that of pure Me$_3$SnCl in the same solvent. This observation suggests that **3** does not retain its structure in pyridine solutions but rather dissociates to give Me$_3$SnCl·py and possibly solvent-stabilized molecules of the digallacyle.[17,18]

Table 1. Crystal Data, Data Collection, and Structure Refinement for 3 and 4

	3−toluene	**4**−toluene
	Crystal Data	
formula	$C_{53}H_{50}Cl_6Ga_4Sn_2$	$C_{67}H_{44}Cl_2Ga_6O_2$
M_r	1415.89	685.12
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$
a (Å)	10.2387(14)	14.1965(9)
b (Å)	10.6114(15)	10.8316(7)
c (Å)	14.112(2)	17.6306(11)
α (deg)	78.677(2)	90
β (deg)	69.505(2)	99.4980(10)
γ (deg)	71.642(2)	90
V (Å^3)	1356.7(3)	2673.9(3)
ρ_{calc} (g·cm^{-3})	1.733	1.702
Z	1	2
F(000) (e)	694	1364
μ(Mo K) (mm^{-1})	3.194	3.128
	Data Collection	
cryst size (mm^3)	0.67 × 0.49 × 0.52	0.76 × 0.28 × 0.17
T (K)	110(2)	110(2)
scan mode	ω	ω
hkl range	−10→12, −12→12, −16→15	−16→13, −12→12, −20→20
no. of measd reflns	10 646	13 423
no. of unique reflns, [R_{int}]	5872, [R_{int} = 0.0382]	4705, [R_{int} = 0.0179]
no. of reflns used for refinement	5872	4239
abs corr	ψ-scan	Sadabs
T_{min}/T_{max}	0.984/0.649	0.574731
	Refinement	
refined params	298	336
final R values [$I > 2\sigma(I)$]		
R1[a] (%)	0.0312	0.0494
wR2[b] (%)	0.0845	0.1388
ρ_{fin}(max/min) (e·Å^{-3})	0.954/−1.177	2.789/−0.835

[a] $R1 = \sum(F_o - F_c)/\sum F_o$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0612 (**3**), 0.1011 (**4**), b = 1.3991 (**3**), 1.7511 (**4**).

When carried out at 25 °C, the reaction of **1** with GaCl$_3$ in toluene led to high yield of **2** (40−55% yield) but also afforded crystals of a new compound (**4**)

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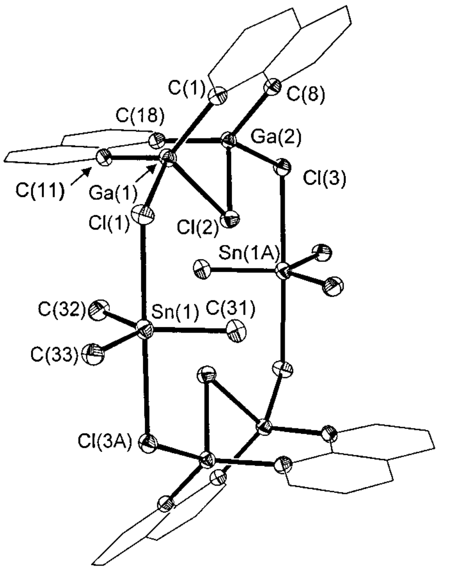

Figure 1. Structure of **3** in the crystal. Selected bond lengths (Å) and angles (deg): Sn(1)−C(33) 2.114(3), Sn(1)−C(31) 2.115(3), Sn(1)−C(32) 2.124(3), Sn(1)−Cl(1) 2.7444(7), Sn(1)−Cl(3A) 2.7578(7), Ga(1)−C(11) 1.955(3), Ga(1)−C(1) 1.957(3), Ga(1)−Cl(1) 2.2806(7), Ga(1)−Cl(2) 2.3803(7), Ga(2)−C(18) 1.962(3), Ga(2)−C(8) 1.965(3), Ga(2)−Cl(3) 2.2723(7), Ga(2)−Cl(2) 2.3743(7); C(33)−Sn(1)−C(31) 121.19(12), C(33)−Sn(1)−C(32) 115.34(12), C(31)−Sn(1)−C(32) 123.35(11), Cl(1)−Sn(1)−Cl(3A), 176.64(2), C(11)−Ga(1)−C(1) 132.28(11), Cl(1)−Ga(1)−Cl(2) 100.07(3), C(18)−Ga(2)−C(8) 134.43(11), Cl(3)−Ga(2)−Cl(2) 100.89(2), Ga(1)−Cl(1)−Sn(1) 111.73(3), Ga(2)−Cl(2)−Ga(1) 76.91(2), Ga(2)−Cl(3)−Sn(1A) 115.28(3).

(Scheme 1). Crystals of **4** are colorless planks that can be physically separated on the basis of their appearance. The yield of compound **4** could be greatly enhanced by adding water to the reaction mixture. Initial optimization of this reaction was done empirically, and the best yields (up to 16%) were obtained for reaction mixtures containing **1**, $GaCl_3$, and H_2O in 0.06, 0.06, and 0.012 M concentration, respectively. Higher concentration of water did not result in higher yields; rather it led to increased formation of naphthalene. As shown, by X-ray analysis (Table 1), elemental analysis, and NMR, **4** is a 12-membered macrocycle containing three gallium atoms linked by 1,8-naphthalenediyl ligands and arranged about a central oxygen atom. The charge balance is achieved by the presence of a chloride atom that occupies a bridging position between two of the gallium centers (Figure 1). In the crystal, **4** exists as a dimer wherein the monomers are bridged via a Ga−O−Ga−O four-membered ring involving Ga(1) (Figure 2). Consequently, the oxygen is four-coordinate and adopts a distorted tetrahedral geometry (97.04° ≤ Ga−O−Ga ≤ 124.48°). A Ga_3O unit constitutes the core of each monomer. In this unit, the Ga−O distances (av 1.95 Å) are shorter than the intermolecular Ga(1)−O(A) distance of 2.028 Å. These distances fall within the range observed for other gallium species featuring multiply bridging oxygen atoms.[19] Each gallium center adopts a distorted tetrahedral geometry. While two naphthalene rings, the oxygen atom, and the bridging chloride occupy the coordination sphere of Ga(2) and Ga(3), the coordination sphere of Ga(1) comprises two naphthalene rings and two oxygen atoms. In each case, the largest deviation from an ideal geometry occurs in the C−Ga−C angle (av 133.2°) as well as in the O−Ga−Cl (av 80.9°) and the O−Ga(1)−O(A) angles (83.0(1)°). The Ga−Cl bonds (av 2.47 Å) are longer than those observed for the bridging chloride in the structure of **3** (av 2.38 Å), suggesting a weaker coordination of the halide ligand. Finally, the three gallium atoms are separated by approximately 3 Å and form a nearly equilateral triangle.

Compound **4** dissolves only in polar solvents such as THF to yield non-conducting solutions. In an effort to understand the structure of **4** in solution, a number of physical measurements have been carried out. Pulse field gradient spin−echo (PGSE) has emerged as a valid method for the determination of diffusion coefficients and hydrodynamic radii of organometallic compounds.[20] Moreover, it has been demonstrated that an excellent correlation exists between the molecular radius derived from X-ray diffraction data and the hydrodynamic radius derived from diffusion determination by PGSE.[21] Thus, to evaluate the radius of **4** in solution, we decided to compare its diffusion to that of two standards, namely, bis(diphenylphosphino)cyclopentadiene iron(II) (**A**)[22] and ETHANOX 330 (**B**).[23] These two standards were chosen because their molecular radii (5.5 Å for **A** and 6.6 Å for **B**), which can be calculated from their crystal structures,[22,23] are close to those of monomeric **4** (5.5−5.75 Å)[24] and dimeric **4** (6.6 Å),[24] respectively. Several measurements were carried out. In all cases, **4** was found to diffuse faster than **B** and slower than **A**. These results suggest that, in solution, **4** undergoes a rapid monomer−dimer equilibrium that leads to the observation of an intermediate molecular size. This view is supported by VT ^1H NMR studies in THF-d_8 which reveal the existence of a fluxional system (Figure 3). The room-temperature spectrum exhibits three sharp signals (two doublets and one pseudo-triplet). Upon cooling to −70 °C, each of the three sharp signals decoalesces into three signals. The rates of exchange at the different temperatures were calculated by line shape analysis techniques.[25] The resulting rates of exchange were used to generate an Eyring plot. A least-squares fit of the resulting plot yielded the activation enthalpy ($\Delta H^{\ddagger} = 43 \pm 3$ kJ·mol^{-1}) and activation entropy ($\Delta S^{\ddagger} = -36 \pm 9$ J·K^{-1}·mol^{-1}). As a whole, these results can be rationalized by invoking the existence of an exchange between the monomeric and dimeric form of **4**. The low-

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[24] These values are obtained by compounding the molecular volume of one or two THF molecules (V_{mol}(THF) = 100 Å^3) with the estimated molecular volume of the ligand-free monomer. The volume of the ligand-free monomer is taken as half of the volume of the dimer. The volume of dimeric **4** (V_{mol}(dimeric **4**) = (V_{cell}/Z) − V_{mol}(toluene) = 1190 Å^3) is deduced from the cell measurement after subtraction of the solvate toluene component (V_{mol}(toluene) = 145 Å^3).

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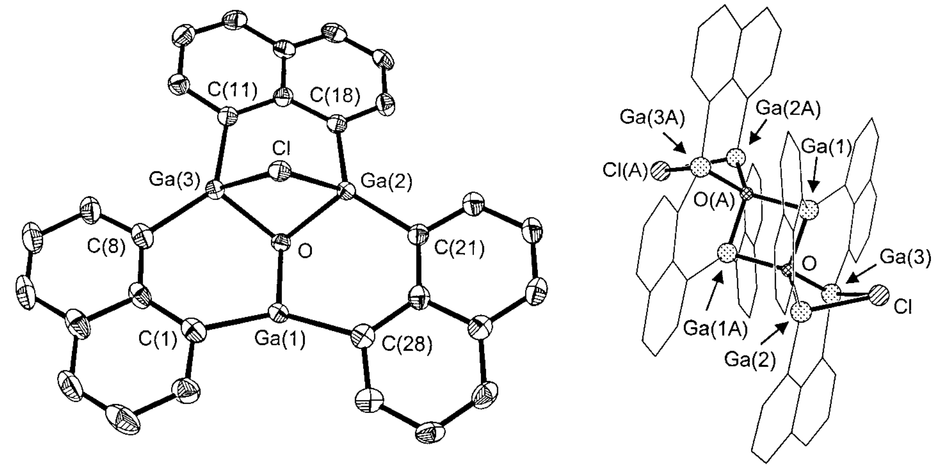

Figure 2. Structure of **4** in the crystal. View of the monomeric unit (left) and the dimer (right). Selected bond lengths (Å) and angles (deg): Sn(1)–Cl(2) 2.740(3), Sn(1)–Cl(1) 2.772(3), Sn(2)–Cl(4) 2.743(3), Sn(2)–Cl(5) 2.751(3), Ga(1)–C(1) 1.957(10), Ga(1)–C(11) 1.970(10), Ga(1)–Cl(1) 2.257(3), Ga(1)–Cl(6) 2.370(3), Ga(2)–C(31) 1.936(12), Ga(2)–C(21) 1.966(11), Ga(2)–Cl(2) 2.279(3), Ga(2)–Cl(3) 2.396(3), Ga(3)–C(38) 1.972(11), Ga(3)–C(28) 1.979(11), Ga(3)–Cl(4) 2.289(3), Ga(3)–Cl(3) 2.379(3), Ga(4)–C(8) 1.951(10), Ga(4)–C(18) 1.984(11), Ga(4)–Cl(5) 2.281(3), Ga(4)–Cl(6) 2.365(3); Cl(2)–Sn(1)–Cl(1) 176.72(9), Cl(4)–Sn(2)–Cl(5) 176.53(9), C(1)–Ga(1)–C(11) 134.1(4), C(1)–Ga(1)–Cl(1) 105.8(4), C(11)–Ga(1)–Cl(1) 104.8(3), C(1)–Ga(1)–Cl(6) 104.3(3), C(11)–Ga(1)–Cl(6) 102.0(3), Cl(1)–Ga(1)–Cl(6) 101.64(11), C(31)–Ga(2)–C(21) 132.7(4), C(31)–Ga(2)–Cl(2) 107.2(3), C(21)–Ga(2)–Cl(2) 106.7(3), C(31)–Ga(2)–Cl(3) 103.7(3), C(21)–Ga(2)–Cl(3) 102.0(4), Cl(2)–Ga(2)–Cl(3) 99.78(10), C(38)–Ga(3)–C(28) 134.5(4), C(38)–Ga(3)–Cl(4) 106.2(4), C(28)–Ga(3)–Cl(4) 105.9(4), C(38)–Ga(3)–Cl(3) 101.9(3), C(28)–Ga(3)–Cl(3) 103.2(3), Cl(4)–Ga(3)–Cl(3) 100.19(11), C(8)–Ga(4)–C(18) 131.6(4), C(8)–Ga(4)–Cl(5) 106.3(3), C(18)–Ga(4)–Cl(5) 106.1(3), C(8)–Ga(4)–Cl(6) 103.9(4), C(18)–Ga(4)–Cl(6) 104.4(3), Cl(5)–Ga(4)–Cl(6) 100.35(11), Ga(1)–Cl(1)–Sn(1) 114.99(11), Ga(2)–Cl(2)–Sn(1) 112.14(12), Ga(3)–Cl(3)–Ga(2) 76.51(9), Ga(3)–Cl(4)–Sn(2) 115.55(11), Ga(4)–Cl(5)–Sn(2) 111.30(12), Ga(4)–Cl(6)–Ga(1) 77.32(9).

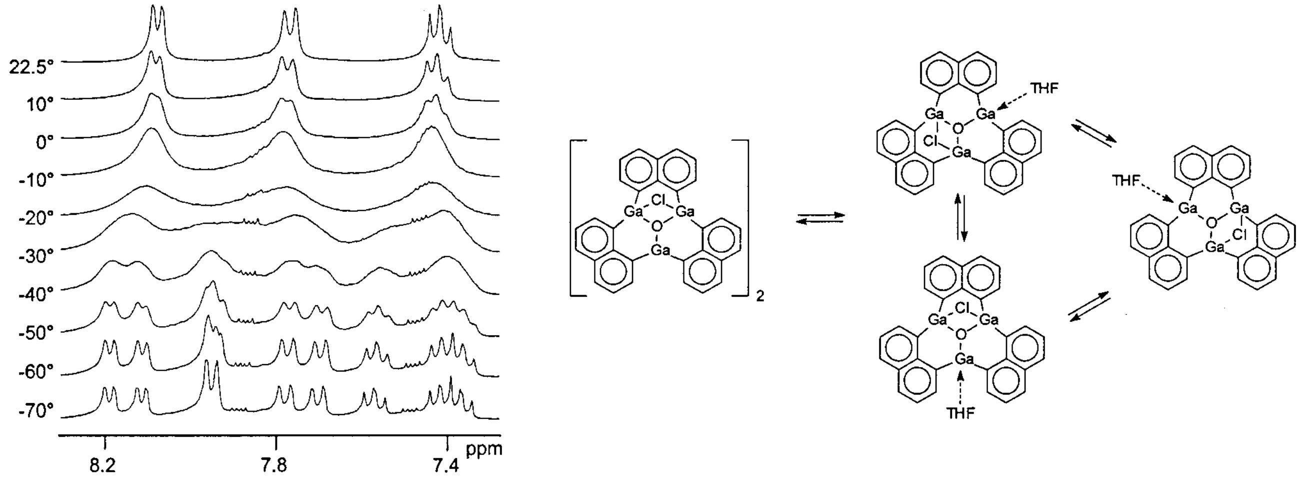

Figure 3. Left: ^{1}H NMR spectra of **4** in THF-d_8 between −70 and +22.5 °C. Right: Proposed exchange process.

temperature spectrum would correspond to that of the dimer as observed in the solid state. The high-temperature data suggest that upon dissociation into the monomer, the chloride anion undergoes rapid exchange, leading to an apparent 3-fold molecular symmetry. In agreement with the lack of conductivity, we propose that the chloride exchange is intra- rather than intermolecular (Figure 3).

Conclusion

The results presented herein indicate that distannanes constitute valuable starting materials for the preparation of polyfunctional organogallium species. In light of the scarcity of macrocyclic species containing several group 13 elements, the serendipitous yet reproducible formation of **4** is noteworthy. Present efforts are focused on the use of **4** as a receptor for polynuclear anions.

Experimental Section

General Procedures. All experimental manipulations were carried out under a N_2 atmosphere using standard Schlenk procedures and a glovebox. NMR spectra were recorded on a Varian VXR-300 instrument at 298 K. The chemical shifts are reported in ppm relative to $SiMe_4$ for ^{1}H/^{13}C and $SnMe_4$ for ^{119}Sn nuclei. Atlantic Microlab (Norcross, GA) performed the elemental analyses. All melting points were measured on samples in sealed capillaries and are uncorrected. Pyridine, toluene, and THF were dried over CaH_2, K, and Na/K, respectively, and distilled before use. Compound **1** was prepared by following the published procedure.[12] Sodium tetraphenylborate was purchased from Aldrich and used without further purification.

Synthesis of 3. A cold (−25 °C) solution of gallium trichloride (97 mg, 0.55 mmol) in toluene (1.5 mL) was added to a cold (−25 °C) solution of **1** (250 mg, 0.55 mmol) in toluene (3 mL). The resulting solution was kept at −25 °C for several days, after which a precipitate formed. The precipitate is a mixture of crystals of **2** and **3**−toluene, which were separated on the basis of morphology. Crystals of **2** are irregular and golden-brown and are isolated in a 21% yield (30 mg). Crystals of **3**−toluene are clear, colorless, and exhibit a cubic shape. Yield of **3**−toluene: 10% (20 mg); mp 72−76 °C dec. Analytical data for **3**-toluene: Anal. Calcd for $C_{53}H_{50}Cl_6Ga_4Sn_2$: C, 44.9; H, 3.56. Found: C, 44.2; H, 3.50. ^{1}H NMR (300 MHz, pyridine-d_5, 25 °C, TMS): δ 0.89 (s with satellites, $^2J(\mathrm{H}-^{119/117}\mathrm{Sn}) =$ 65/68 Hz, 9H, CH_3), 7.52 (*pseudo*-t, ^3J(H,H) = 7.3 Hz, 7.6 Hz, 4H, C*H*(3,6)), 7.96 (d, ^3J(H,H) = 7.8 Hz, 4H, C*H*(4,5)), 8.62 (d, ^3J(H,H) = 6.6 Hz, 4H, C*H*(2,7)). ^{13}C NMR (75 MHz, pyridine-d_5, 25 °C, TMS): δ 125.3 (*C*-3,6), 130.4 (*C*-4,5), 134.7 (*C*-10), 138.8 (*C*-2,7), 145.2 (*C*-9), 160.4 (*C*-1,8). ^{119}Sn NMR (149.03 MHz, pyridine-d_5): δ −16.0.

Synthesis of 4. A solution of gallium trichloride (49 mg, 0.28 mmol) in toluene (1.5 mL) was added to a solution of **1** (125 mg, 0.28 mmol) in toluene (3 mL) containing water (1.0 μL, 56 μmol). The resulting solution was left in a vial in a glovebox for 2 days, after which a powder of **4**−toluene had precipitated. Yield: 16% (10 mg); mp 195 °C dec. Anal. Calcd for $C_{67}H_{44}O_2Cl_2Ga_6$: C, 58.7; H, 3.2. Found: C, 58.3; H, 3.2. ^{1}H NMR (300 MHz, THF-d_8, 25 °C, TMS): δ 7.43 (*pseudo*-t, ^3J(H,H) = 6.6 Hz, 8.1 Hz, 6H, C*H*(3,6)), 7.79 (d, ^3J(H,H) = 7.8 Hz, 6H, C*H*(4,5)), 8.10 (d, ^3J(H,H) = 6.6 Hz, 6H, C*H*(2,7)).

Single-Crystal X-ray Analysis. The crystallographic measurements were performed at $T = 110$ K using a Siemens SMART-CCD area detector diffractometer, with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Specimens of suitable size and quality were selected and mounted onto a glass fiber with Apiezon grease. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. All hydrogen atoms were included in calculated positions using a standard riding model. In the structure of **3**, however, the disordered hydrogen atom attached to C(41) was not included in the refinement. Further crystallographic details can be found in Table 1 and in the Supporting Information.

Pulsed Field Gradent Spin−Echo NMR. All measurements were performed on a Varian Inova 500 MHz spectrometer using Varian's diffusion software package. Samples were recorded in THF-d_8 at 293 K without spinning. During an experiment, all factors were kept constant while the gradient strength (G) was arrayed between 0 and 14 G/cm. The gradient was calibrated using D_2O. Following data collection, the spectra were carefully integrated. The resulting data points were subjected to a least-squares fit which produced, as per eq 1, a regression line whose slope is proportional to the diffusion coefficient and inversely proportional to the molecular hydrodynamic radius.

$$\ln\left(\frac{I}{I_0}\right) = -\gamma\delta^2G^2\left(\Delta - \frac{\delta}{3}\right)D \qquad (1)$$

Two standards (**A**[22] and **B**[23]) with crystallographic radii ($R_{\mathrm{X-ray}}$) and therefore hydrodynamic radii (R_{H})[21] approaching those expected for monomeric **4** and dimeric **4**, respectively, were selected. The slope obtained for **4** was compared to those of the two standards. In all measurements, the slope obtained for **4** was well between those of **A** and **B**.

Variable-Temperature NMR. Proton NMR spectra of **4** in THF obtained at −70, −60, −50, −40, −30, −20, −10, 0, 10, and 22.5 °C could be successfully simulated with the program gNMR 4.1. The resulting exchange rate constants were used to generate an Eyring plot, which yielded $\Delta H^\ddagger =$ 43 ± 3 kJ·mol^{-1} and $\Delta S^\ddagger = -36 \pm 9$ J·K^{-1}·mol^{-1}.

Conductivity Measurements. The cell constant of a YSI Model 35 conductance meter was determined by conductivity measurement of a 0.02 M KCl solution in distilled water and found to be 1.0855. To assess the reliability of the measurement, THF solutions of sodium tetraphenylborate were prepared and their conductivity was measured. The conductance values obtained from these solutions were in close agreement with those previously reported in the literature.[26] THF solutions of **4** at concentrations of 1.67×10^{-3}, 8.33×10^{-4}, 4.17×10^{-4}, 2.08×10^{-4}, and 1.04×10^{-4} M were prepared in a dry N_2 atmosphere and transferred to the cell. The cell was sealed and connected to the conductance meter for measurement. The conductivity of these solutions did not differ from that of pure THF within experimental error.

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Supporting Information Available: Spectral data and tables of structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for complexes **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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