uent compared to that of the alkyl group. No data from such studies need to be interpreted in terms of any significant π bonding between the metal and silicon atoms.[21]

It is reported that for the Re–Me complex, no B_1 band and a single E mode band are observed due to the symmetric top nature of the Me group.[22] We note that no B mode band is observed for the disilyl and trisilyl groups, but the E mode band is split. The silylmethyl and disilylmethyl complexes exhibit both E mode splitting and the appearance of a B_1 mode band. In the case of the Rp complexes both the symmetric and antisymmetric bands are of equivalent intensity, indicating that the OC–Ru–CO bond angle is $\simeq 90°$ for all the complexes and that steric features of the varying $(Si)_n$ groups do not change the geometry at the metal center.

Reactivity. In contrast to the Fp–disilyl and –trisilyl complexes, irradiation of the Ru and Re polysilyl complexes with a 500-W Hanovia lamp gave no deoligomerization (<1%) after 48 h. In the case of the related Fp complexes, under identical conditions, irradiation for time periods as short as 2 h will give complete deoligomerization. It is not clear what is the root cause for such distinction between the Fp complexes and the two sets of complexes reported here. In the case of the Fp complexes, we have suggested that the initial step in the photochemical deoligomerization is the loss of a CO ligand to produce a reactive $16e^-$ system. It appears that the Ru and Re complexes are significantly resistant to CO expulsion under the conditions reported here.

Migrations of silyl groups from Fe to the cyclopentadienyl ring in $Fp–SiR_3$ complexes has been effected by base treatment, *n*-BuLi or $Li(i\text{-}Pr)_2N$.[5,23,24] These reactions involve initial deprotonation on the cyclopentadienyl ring, followed by migration of the silyl group to the ring with the formation of an Fe centered ion, which may be trapped by, inter alia, MeI. We have performed a similar reaction with $Rp–SiMe_3$ and find that an exactly analogous reaction takes place involving migration of the Me_3Si group from Ru to the cyclopentadienyl ring. The mechanism is presumably the same as that for the Fp complexes.

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Registry No. $Rp–SiMe_3$, 43184-26-5; $Rp–SiMe_2SiMe_3$, 109584-80-7; $Rp–SiMe_2SiMe_2SiMe_3$, 109584-81-8; $Rp–SiMe(SiMe_3)_2$, 109584-82-9; $Rp–CH_2SiMe_2Me_3$, 109584-83-0; $Rp–CH_2SiMe_3$, 109584-84-1; $LM–SiMe_2SiMe_3$, 36632-62-9; RpK, 84332-45-6; $(Rp)_2$, 12132-87-5; $Re_2(CO)_{10}$, 14285-68-8; $Na_2[Re_2(CO)_9]$, 109584-85-2; $ClSi_2Me_5$, 1560-28-7; $LM–SiMe_3$, 55208-33-8; $LM–SiMe_2SiMe_2SiMe_3$, 109584-86-3; $LM–SiMe(SiMe_3)_2$, 109584-87-4; $LM–CH_2SiMe_3$, 109584-88-5; $LM–CH_2SiMe_2SiMe_3$, 109584-89-6; $ClCH_2Me_5Si_2$, 5181-46-4; $ClSiMe_2SiMe_2SiMe_3$, 918-19-4; $(Me_3Si)_2SiMeCl$, 754-38-1; Me_3SiCl, 75-77-4; Me_6Si_2, 1450-14-2; $ClCH_2SiMe_3$, 2344-80-1; $(C_5H_4SiMe_3)\,Ru(CO)_2Me$, 109584-90-9; ^{29}Si, 14304-87-1.

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Synthesis and Characterization of Mesitylgallium Chloride Compounds Including the Crystal and Molecular Structure of Dichloromesitylgallium(III), an Inorganic Polymer

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The mesitylgallium chloride compounds $GaMes_2Cl$ and $GaMesCl_2$ have been prepared and fully characterized by melting point data, elemental analyses, solubility properties, IR and ^1H and ^{13}C NMR spectroscopic data, and Lewis acidity studies. Cryoscopic molecular weight studies of $GaMes_2Cl$ in benzene solution are consistent with the presence of dimeric molecules. Lewis bases such as Et_2O and THF react with $(GaMes_2Cl)_2$ in benzene to establish two equilibria which are consistent with the presence of the dimer, a monochloride bridged 2:1 adduct $[(GaMes_2Cl)_2\cdot base]$, and the 1:1 adduct. The dichloro derivative $GaMesCl_2$ is an unusually high melting solid which is insoluble in hydrocarbon solvents and crystallizes in the centrosymmetric monoclinic space group $P2_1/m$ (C_{2h}^2; No. 11) with $a = 8.3989$ (21) Å, $b = 6.9976$ (19) Å, $c = 18.0347$ (57) Å, $\beta = 100.159$ (23)°, $V = 1043.3$ (5) Å^3, and $Z = 4$ (formula units). Diffraction data (Mo Kα, $2\theta = 5.0$–$45.0°$) were collected with a Syntex $P2_1$ diffractometer, and the structure was refined to $R_F = 6.2\%$ for all 1502 independent reflections. Dichloromesitylgallium(III) is a one-dimensional polymer in which planar GaMesCl (Mes = mesityl) units are linked by bridging chloride ligands. The correct formulation is $[Ga(C_6H_2Me_3)Cl(\mu\text{-}Cl)]_\infty$. Distances of interest include Ga···Ga = 3.781 (1) Å, Ga–Cl(terminal) = 2.150 (4)–2.164 (4) Å, Ga–Cl(bridging) = 2.363 (3)–2.369 (3) Å, and Ga–C(mesityl) = 1.943 (12)–1.970 (14) Å.

Introduction

The presence of bulky organic substituents on main-group elements leads to a variety of interesting and unusual chemical properties. Four mesityl (Mes) groups served to stabilize the first fully characterized compound with a silicon–silicon double bond,[1] Si_2Mes_4. In group 13 chemistry, the effects of bulky substituents are just beginning to be elucidated. In indium(I) chemistry, the bulky pen-

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tamethylcyclopentadienyl group produced a hydrocarbon soluble, golden yellow solid which had a structure based upon an apparent octahedral cluster of $In_6(C_5Me_5)_6$ with indium(I) atoms on the interior and η^5-C_5Me_5 groups on the exterior.[2] In contrast, $In(C_5H_5)$ has been described as a hydrocarbon-insoluble, yellow solid with a zigzag polymeric structure.[3] When the typical compounds of the heavier group 13 elements are considered, the primary effects of the bulky substituents appear to be related to a reduction in their Lewis acidity. Triorganoaluminum compounds such as $AlMe_3$[4] and $AlPh_3$[5] are dimers, but $Al(t\text{-}Bu)_3$[6] and $AlMes_3$[7] are monomers. The X-ray structural study of $AlMes_3$ reveals significant interactions between ortho methyl groups.[7] Trimesitylgallium[8] is also monomeric in the solid state, but this is not surprising because even $GaMe_3$ is a monomer.[9] However, the Lewis acidity[8] of $GaMes_3$ has been reduced so significantly that it does not form adducts with Et_2O or the stronger base THF. Similar observations[10] have been made for $Ga(C_5Me_5)_3$. Two pentamethylcyclopentadienyl groups on gallium also have significant effects. The compound $Ga(C_5Me_5)_2Cl$ is monomeric in benzene solution,[11] and it does not form Et_2O or THF adducts. However, the two C_5Me_5 groups are insufficient to prevent the formation of the typical dimer with chlorine bridges in the solid state. When the number of pentamethylcyclopentadienyl groups is reduced to one,[11] all properties of $Ga(C_5Me_5)Cl_2$ are consistent with an organogallium compound with small substituents.

In this paper, the synthesis and characterization of $GaMes_2Cl$ and $GaMesCl_2$ are described. The characterization data for both compounds include melting points, elemental analyses, solubility properties, IR and ^1H and ^{13}C NMR spectroscopic data, and Lewis acidity studies. In addition, the X-ray structural study of $GaMesCl_2$ is described. The presence of bulky mesityl groups leads to unexpected observations. The compound $GaMesCl_2$ exists in the crystalline state as a linear chloride-bridged polymer, a novel structure in group 13 chemistry. The dimesityl derivative $GaMes_2Cl$ reacts with the Lewis base diethyl ether to establish equilibria involving a minimum of three dimesitylgallium species.

Experimental Section

General Data. All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. Gallium(III) chloride was purified by sublimation under high vacuum at 70–80 °C immediately prior to use. Trimesitylgallium(III) ($GaMes_3$) was prepared as previously described.[8] All solvents were purified prior to use. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with abbreviations w (weak), m (medium), s (strong), vs (very strong), and sh (shoulder). The ^1H NMR spectra were recorded at 90 MHz by using a Varian Model EM-390 spectrometer. Chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at δ 0.00 and benzene at δ 7.13. The ^{13}C NMR spectra were recorded at 22.49 MHz by using a JEOL FX-90Q spectrometer. Carbon-13 chemical shifts are referenced to dioxane at δ 66.5. All NMR tubes were sealed under vacuum. Molecular weights were measured cryoscopically in benzene solution by using an instrument similar to that described by Shriver.[12]

Synthesis of $GaMes_2Cl$. In a typical experiment, recrystallized $GaMes_3$ (2.469 g, 5.78 mmol) and $GaCl_3$ (0.508 g, 2.89 mmol) were placed in a 100-mL flask equipped with a Solv-Seal joint. Diethyl ether, 50 mL, was vacuum distilled onto the mixture of $GaMes_3$ and $GaCl_3$, and the reaction mixture was permitted to warm to room temperature. The resulting colorless solution was then stirred for 18 h, after which time it was filtered through a fine glass frit. After the ether was removed by vacuum distillation, trace quantities of Et_2O and/or vacuum grease were removed by washing the product with one 40-mL portion of pentane. Additional $GaMes_2Cl$ was obtained from the pentane-soluble portion to yield dimesitylgallium(III) chloride, $GaMes_2Cl$ (2.396 g, 6.974 mmol, 80.5% yield), as a colorless powder. If additional purification of $GaMes_2Cl$ is desired, the compound can be recrystallized from pentane.

$GaMes_2Cl$: mp 158–159.5 °C. Anal. Calcd: C, 62.93; H, 6.45; Cl, 10.32. Found: C, 62.99; H, 6.38; Cl, 10.39. ^1H NMR (C_6D_6, δ): 6.62 (aromatic H, 2 H), 2.40 (ortho Me, 6 H), 2.07 (para Me, 3 H); ^1H NMR (THF-d_8, δ): 6.68 (aromatic H, 2 H), 2.39 (ortho Me, 6 H), 2.15 (para Me, 3 H). ^{13}C NMR ($C_4H_8O_2$, δ): 143.73 (β-aromatic C), 140.95 (α-aromatic C), 137.64 (δ-aromatic C), 127.79 (γ-aromatic C), 24.03 (ortho Me), 20.03 (para Me). IR (Nujol mull, cm^{-1}): 1755 vw, 1731 vw, 1720 vw, 1598 s, 1550 m, 1404 m, 1287 m, 1237 w, 1226 w, 1025 m, 950 vw, 943 w, 886 vw, 875 w, 853 m, 841 vs, 718 w, 704 w, 682 vw, 587 s, 562 m, 540 s, 496 w, 489 w, 344 m, 335 m, 320 m, 280 m, 263 m, 244 vs. Solubility: soluble in Et_2O, THF, and benzene; slightly soluble in pentane. Cryoscopic molecular weight, formula weight $GaMes_2Cl$, 344 (obsd mol wt, obsd molality, association): 696, 0.0364, 2.03; 679, 0.0285, 1.98; 679, 0.0209, 1.98.

Synthesis of $GaMesCl_2$. A benzene solution (5 mL) of 1.308 g of $GaMes_3$ (3.061 mmol) was added by means of a side-arm dumper to a flask charged with 1.079 g of $GaCl_3$ (6.130 mmol) dissolved in 45 mL of benzene. Initially, the reaction mixture was a colorless solution. However, within 15 min a small amount of white precipitate was observed. The reaction mixture was then stirred for 18 h during which time a heavy white precipitate formed. The benzene was then removed by vacuum distillation, and the white powder was washed with pentane to facilitate the removal of trace quantities of benzene. Within a few hours of the removal of the pentane and while the flask was still under high vacuum, the color of the product changed from white to slightly "off-white". Mesitylgallium(III) dichloride, $GaMesCl_2$, was isolated as an "off-white" powder (2.041 g, 7.856 mmol, 84.5% yield). The compound $GaMesCl_2$ may be further purified by vacuum sublimation at 140 °C; however, the sublimation product still maintains its "off-white" appearance. Colorless crystals of $GaMesCl_2$ suitable for X-ray analysis were grown by slow sublimation in a sealed tube at 126 °C.

$GaMesCl_2$: mp 199.0–201.5 °C. Anal. Calcd: C, 41.61; H, 4.27; Cl, 27.29. Found: C, 41.78; H, 4.47; Cl, 27.23. ^1H NMR (THF-d_8, δ): 6.74 (aromatic H, 2 H), 2.48 (ortho Me, 6 H), 2.20 (para Me, 3 H). ^{13}C NMR ($C_4H_8O_2$, δ): 144.56 (β-aromatic C), 138.86 (δ-aromatic C), 133.30 (α-aromatic C), 128.03 (γ-aromatic C), 23.93 (ortho Me), 20.08 (para Me). Solubility: soluble in Et_2O and THF; insoluble in benzene and pentane. IR (Nujol mull, cm^{-1}): 1725 vw, 1594 m, 1552 w, 1409 w, 1290 m, 1240 w, 1156 vw, 1037 m, 880 vw, 842 vs, 830 vw, 719 w, 698 w, 682 vw, 671 w, 589 m, 560 vw, 540 m, 520 w, 492 vw, 396 vs, 365 sh, 330 sh, 313 w, 278 w. Crystals of $GaMesCl_2$ are extremely sensitive to air as evidenced by a rapid color change to brown.

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Table I. Experimental Data for the X-ray Diffraction Study of Dichloromesitylgallium(III)

(A) Crystal Parameters at 24 °C (297 K)

cryst system: monoclinic
space group: $P2_1/m$ (C_{2h}^2; No. 11)
$a = 8.3989$ (21) Å
$b = 6.9976$ (19) Å
$c = 18.0347$ (57) Å
$\beta = 100.159(23)°$
$V = 1043.3$ (5) Å^3
$Z = 4$ formula units
fw = 259.8 amu
ρ(calcd) = 1.65 g cm^{-3}

(B) Data Collection

diffractometer: Syntex $P2_1$
radiation: Mo K$\bar{\alpha}$ ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: highly oriented (pyrolytic) graphite, mounted in equatorial mode with 2θ(m) = 12.160°; assumed to be 50% perfect/50% ideally imperfect for polarization correction
reflections measured: $+h,\pm k,\pm l$ for $2\theta = 5.0$–$45.0°$; 2956 reflections measured and merged to 1502 point-group independent data: $R(I) = 5.7\%$ for averaging 1250 pairs of reflections
scan conditions: coupled θ(crystal)–2θ(counter) from $[2\theta(K\alpha_1) - 1.1]°$ through $[2\theta(K\alpha_2) + 1.1]°$ at a scan speed of 4.0°/min in 2θ
backgrounds: stationary crystal and counter at beginning and end of the 2θ scan; each for one-half of total scan time
standard reflections: three (142, $52\bar{6}$, 411) collected after each batch of 97 reflections; no decay or instability detected
absorption (μ = 32.3 cm^{-1}): corrected empirically by interpolation (in 2θ and ϕ) between ψ scans of four close-to-axial reflections ($30\bar{2}$ with $2\theta = 14.69°$ and min/max = 0.710; $40\bar{1}$ with $2\theta = 24.51°$ and min/max = 0.735; $60\bar{3}$ with 2θ = 29.40° and min/max = 0.713)

Lewis Acidity Studies of $GaMes_2Cl$ and $GaMesCl_2$. A weighed evacuated tube was charged with either a sample of $GaMes_2Cl$ or $GaMesCl_2$. The tube was evacuated and reweighed to determine the mass of the gallium sample. A large excess of base (THF or Et_2O) was vacuum distilled into the tube. The resulting solution was stirred for 15 min. The excess base was then removed by vacuum distillation, and the system was subjected to dynamic vacuum for an additional 15 h. The tube was reweighed to determine if the change in mass indicated the formation of a stoichiometric adduct. A ^1H NMR spectrum (benzene solution) of the material remaining in the reaction tube was used to confirm the results of the mass measurements. Both $GaMes_2Cl$ and $GaMesCl_2$ formed 1:1 adducts with THF which are stable at room temperature. Neither compound formed a stable 1:1 adduct with Et_2O. $GaMes_2Cl\cdot THF$: mass $GaMes_2Cl$ 0.0705 g, mass THF 0.0144 g, mole ratio $GaMes_2Cl$/THF = 1.03. ^1H NMR (C_6H_6, δ): 3.54 (THF), 2.54, 2.31, 2.16, 2.13, 2.09, 1.15 (THF). $GaMesCl_2\cdot THF$: mass $GaMesCl_2$ 0.0764 g, mass THF 0.0157 g, mole ratio $GaMesCl_2$/THF = 1.35. ^1H NMR (C_6H_6, δ): 3.54 (THF, 4.1), 2.57 (ortho Me, 5.6), 2.11 (para Me, 3.0), 1.02 (THF, 4.1). See Results and Discussion for an explanation of these data.

Collection of X-ray Diffraction Data for Dichloromesitylgallium(III). A transparent colorless crystal of approximate orthogonal dimensions 0.22 × 0.33 × 0.50 mm^3 was selected for the structural analysis and was inserted into a thin-walled glass capillary under an inert atmosphere (Ar). The crystal was mounted and aligned on a Syntex $P2_1$ automated four-circle diffractometer. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out as described previously.[13] Intensity data were collected with Mo Kα radiation for $2\theta = 5.0$–$45.0°$ by using conditions described in Table I. Data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale by means of a Wilson plot. The diffraction symmetry was $2/m$ (C_{2h}) with systematic absences of $0k0$ for $k = 2n + 1$ (only). Possible space groups are the noncentrosymmetric $P2_1$ (C_2^2; No. 4) and the centrosymmetric $P2_1/m$ (C_{2h}^2; No. 11). Data were collected for the quadrants $+h,+k,\pm l$ and for $+h,-k,\pm l$ because of the possibility that b might be a polar axis (i.e., the space group could be $P2_1$). Intensity statistics later suggested that the structure was centric, and this was confirmed by the successful solution of the structure in the higher symmetry centrosymmetric space group $P2_1/m$. (It should be noted that all crystals of $Ga(C_6H_2Me_3)Cl_2$ that we examined, including the data crystal, gave rise to rather broad diffraction peaks characteristic of the crystals' possessing an unusually large mosaic spread; a very accurate structural determination was not anticipated.)

Table II. Final Positional Parameters for $Ga(C_6H_2Me_3)Cl_2$[a,b]

atom	x	y	z
Ga(1)	0.49434 (15)	0.25000 (0)	0.29349 (8)
Ga(2)	0.38263 (15)	−0.25000 (0)	0.22357 (8)
Cl(1)	0.50000 (43)	0.25000 (0)	0.17474 (20)
Cl(2)	0.64035 (38)	−0.25000 (0)	0.26564 (23)
Cl(12)	0.30588 (23)	0.00130 (38)	0.29795 (12)
C(11)	0.6716 (16)	0.25000 (0)	0.38101 (79)
C(12)	0.6351 (14)	0.25000 (0)	0.45549 (71)
C(13)	0.7526 (17)	0.25000 (0)	0.51794 (76)
C(14)	0.9278 (15)	0.25000 (0)	0.50304 (93)
C(15)	0.9483 (16)	0.25000 (0)	0.4336 (11)
C(16)	0.8290 (14)	0.25000 (0)	0.37126 (83)
C(12A)	0.4541 (15)	0.25000 (0)	0.47165 (81)
C(14A)	1.0574 (20)	0.25000 (0)	0.5744 (10)
C(16A)	0.8725 (15)	0.25000 (0)	0.29188 (84)
C(21)	0.2528 (13)	−0.25000 (0)	0.12308 (65)
C(22)	0.3367 (14)	−0.25000 (0)	0.05672 (75)
C(23)	0.2445 (15)	−0.25000 (0)	−0.01389 (73)
C(24)	0.0609 (16)	−0.25000 (0)	−0.02179 (79)
C(25)	0.0025 (17)	−0.25000 (0)	0.0391 (10)
C(26)	0.0852 (17)	−0.25000 (0)	0.11385 (77)
C(22A)	0.5154 (16)	−0.25000 (0)	0.06566 (89)
C(24A)	−0.0434 (20)	−0.25000 (0)	−0.09872 (93)
C(26A)	−0.0079 (13)	−0.25000 (0)	0.17817 (86)
H(12A)	0.4558	0.2500	0.5254
H(12B)	0.3951	0.1391	0.4522
H(13)	0.7500	0.2500	0.5714
H(14A)	1.0100	0.2500	0.6194
H(14B)	1.1257	0.3608	0.5753
H(15)	1.0795	0.2500	0.4300
H(16A)	0.9845	0.2500	0.2937
H(16B)	0.8275	0.3608	0.2632
H(22A)	0.5806	−0.2500	0.0145
H(22B)	0.5551	−0.3608	0.0946
H(23)	0.2744	−0.2500	−0.0618
H(24A)	0.0203	−0.2500	−0.1368
H(24B)	−0.1119	−0.1391	−0.1037
H(25)	−0.0731	−0.2500	0.0754
H(26A)	0.0630	−0.2500	0.2337
H(26B)	−0.0761	−0.3608	0.1730

[a] Hydrogen atoms are in idealized calculated positions; those of the methyl groups are based upon the locations of hydrogen atoms observed at $y = +^1/_4$ and $-^1/_4$. [b] B(iso) = 6.0 Å^2 for hydrogen atoms.

Solution and Refinement of the Structure of Dichloromesitylgallium(III). All crystallographic calculations were carried out by using our locally modified form of the Syntex XTL package of crystallographic programs. Calculated structure factors were derived from the analytical expression of the scattering factors for neutral atoms; $\Delta f'$ and $i\Delta f''$ terms were included for all atoms.[14] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $1/w = \{[\sigma(|F_o|)]^2 + [0.015|F_o|]^2\}$.

The structure was solved by direct methods (MULTAN)[15] in space group $P2_1/m$ using parity-group renormalized $|E|$ values. An "E map" provided the positions of two independent gallium atoms in special positions 0.497, $^1/_4$, 0.295 and 0.382, $-^1/_4$, 0.222. The remaining non-hydrogen atoms were located from difference Fourier syntheses. Refinement of positional and isotropic thermal parameters for all non-hydrogen atoms converged with R_F = 10.4%. The use of anisotropic thermal parameters and the inclusion of hydrogen atoms in calculated positions[16] led to con-

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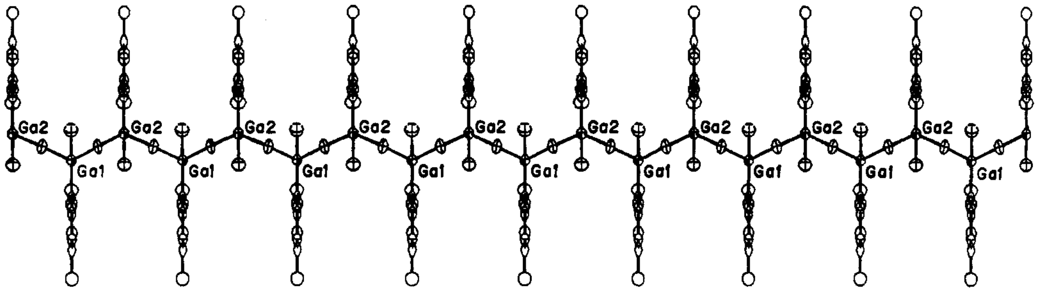

Figure 1. The polymeric structure of dichloromesitylgallium(III). [The *b* axis is horizontal with a repeat distance of 6.998 (2) Å.] The angles Ga(2)···Ga(1)···Ga(2) (x, $1 + y$, z) and Ga(1)···Ga(2)···Ga(1) (x, $-1 + y$, z), which define the kink in the zigzag polymer, are equivalent at 135.46 (4)°.

vergence with $R_F = 6.2\%$ for 142 variables refined against 1502 observed reflections. [$R_F = 5.7\%$ for those 1231 data with $|F_o| > 6\sigma(|F_o|)$.] A final difference Fourier map showed no unusual features ($\rho(\max) = 1.33$e at 0.148, $^1/_4$, -0.036). Positional parameters are listed in Table II.

Results and Discussion

The mesitylgallium halides $GaMes_2Cl$ and $GaMesCl_2$ have been prepared by stoichiometric ligand redistribution reactions between $GaMes_3$ and $GaCl_3$ and have been isolated in high yields. The two new compounds have been fully characterized by melting points, elemental analyses, solubility properties, cryoscopic molecular weight measurements, and Lewis acidity studies as well as IR and ^{1}H and ^{13}C NMR spectroscopic data. In addition, an X-ray structural study of $GaMesCl_2$ has defined its crystal structure as a one-dimensional polymer.

The synthesis of $GaMes_2Cl$ from a reaction mixture which had a stoichiometry of 2 mol of $GaMes_3$/mol of $GaCl_3$ was facilitated by the use of Et_2O as the reaction solvent. Both reactants and the product were soluble, but the product $GaMes_2Cl$ did not form an adduct. It is also of interest that the final traces of ether were effectively removed by washing the product once with pentane. Pentane has also been attempted as a possible reaction solvent, but its use is not recommended. The limited solubility of both $GaMes_3$ and $GaMes_2Cl$ in pentane hinders the reaction from going to completion. Cryoscopic molecular weight measurements in benzene solution demonstrate that $GaMes_2Cl$ exists as a dimer. Even though an X-ray structural study of this compound is not available, a chloride-bridged dimer would be the most likely structure. This type of structure has been observed by X-ray structural studies of $[Ga(C_5Me_5)_2Cl]_2$,[11] $[Ga(C_5Me_5)Cl_2]_2$,[11] and $(GaCl_3)_2$.[17]

Mesitylgallium dichloride has also been prepared in high yield by a stoichiometric ligand redistribution. Since the product has the stoichiometry of the combined reactants, great care must be taken when weighing and transferring the reactants to the reaction vessel. The preferred solvent for this reaction is benzene because both reagents are readily soluble and benzene has no Lewis base properties to gallium. Diethyl ether was also used as a reaction solvent, but purification of the product was more difficult. The experimental observations after the reagents in a ratio of 1 mol of $GaMes_3$ to 2 mol of $GaCl_3$ were mixed in benzene were most unusual. Initially a clear solution was present. Then, after 15 min a small amount of white precipitate was observed. As the reaction progressed, more and more precipitate formed. These observations suggest that the reactions as shown by eq 1 and 2 are most likely slow. A slow ligand redistribution reaction of $GaMes_3$ would be consistent with its low Lewis acidity due to the steric effects of the bulky mesityl groups.

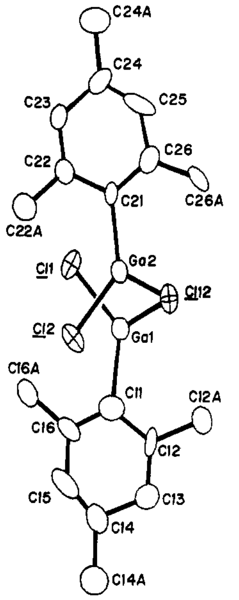

Figure 2. The crystallographic asymmetric unit of dichloromesitylgallium(III) with atomic labeling. The view is perpendicular to that of Figure 1, and the structure extends by Ga(2) linking to a further symmetry-related bridging chloride ligand above the position of Cl(12) and by Ga(1) linking to a further bridging chloride ligand below the position of Cl(12).

$$GaMes_3 + GaCl_3 \rightarrow GaMes_2Cl + GaMesCl_2(s) \qquad (1)$$

$$GaMes_2Cl + GaCl_3 \rightarrow 2GaMesCl_2(s) \qquad (2)$$

The crystal of $GaMesCl_2$ consists of (theoretically infinite) strands of the one-dimensional polymer $[Ga(C_6H_2Me_3)Cl(\mu\text{-}Cl)]_\infty$. There are no short contacts between the strands. A section of one such strand is shown in Figure 1. The crystallographic "repeat unit" and atomic labeling are shown in Figure 2. This consists of a GaMesCl unit at $y = {}^1/_4$ centered on Ga(1) and a GaMesCl unit at $y = -{}^1/_4$ centered on Ga(2) and bridging chloride ligands (Cl(12) at $y \approx 0$ and the symmetry-related Cl(12) (x, $-{}^1/_2 + y$, z) at $y \approx -{}^1/_2$).

Interatomic distances and angles are collected in Table III. The Ga(1)···Ga(2) separation is 3.781 (1) Å, and the stacks of parallel mesityl ligands shown in Figure 1 have a repeat distance of 6.998 (2) Å (i.e., the *b* dimension of the unit cell). Each gallium atom is tetrahedrally surrounded by four groups—a terminal chloride, two bridging chlorides, and an η^1-mesityl ligand. Ga–Cl (terminal) distances are Ga(1)–Cl(1) = 2.150 (4) and Ga(2)–Cl(2) = 2.164 (4) Å (average = 2.157 ± 0.010 Å); the Ga–Cl(bridging) distances are substantially longer with Ga(1)–

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Table III. Selected Interatomic Distances (Å) and Angles (deg) for $Ga(C_6H_2Me_3)Cl_2$

(A) Distances Involving the Gallium Atoms			
Ga(1)···Ga(2)	3.781 (1)	Ga(1)–Cl(1)	2.150 (4)
Ga(1)···Ga(2)[a]	3.781 (1)	Ga(2)–Cl(2)	2.164 (4)
Ga(2)···Ga(1)[b]	3.781 (1)	Ga(1)–C(11)	1.970 (14)
Ga(1)–Cl(12)	2.363 (3)	Ga(2)–C(21)	1.943 (12)
Ga(1)–Cl(12)[c]	2.363 (3)		
Ga(2)–Cl(12)	2.369 (3)		
Ga(2)–Cl(12)[d]	2.369 (3)		
(B) C–C(Ring) Distances within Mesityl Ligands			
C(11)–C(12)	1.43 (2)	C(21)–C(22)	1.49 (2)
C(12)–C(13)	1.36 (2)	C(22)–C(23)	1.37 (2)
C(13)–C(14)	1.54 (2)	C(23)–C(24)	1.52 (2)
C(14)–C(15)	1.29 (3)	C(24)–C(25)	1.28 (3)
C(15)–C(16)	1.37 (2)	C(25)–C(26)	1.40 (2)
C(16)–C(11)	1.36 (2)	C(26)–C(21)	1.39 (2)
(C) C–Me Distances			
C(12)–C(12A)	1.60 (2)	C(22)–C(22A)	1.48 (2)
C(14)–C(14A)	1.53 (2)	C(24)–C(24A)	1.51 (2)
C(16)–C(16A)	1.54 (2)	C(26)–C(26A)	1.51 (2)
(D) Angles around the Gallium Atoms			
Cl(1)–Ga(1)–Cl(12)	99.58 (11)	Cl(2)–Ga(2)–Cl(12)	99.02 (11)
Cl(1)–Ga(1)–Cl(12)[c]	99.58 (11)	Cl(2)–Ga(2)–Cl(12)[d]	99.02 (11)
Cl(1)–Ga(1)–C(11)	130.67 (34)	Cl(2)–Ga(2)–C(21)	133.56 (29)
Cl(12)–Ga(1)–Cl(12)[c]	94.84 (9)	Cl(12)–Ga(2)–Cl(12)[d]	95.85 (9)
Cl(12)–Ga(1)–C(11)	112.88 (34)	Cl(12)–Ga(2)–C(21)	111.36 (28)
C(11)–Ga(1)–Cl(12)[c]	112.88 (34)	C(21)–Ga(2)–Cl(12)[d]	111.36 (28)
(E) Angle at Bridging Chloride Ligand			
Ga(1)–Cl(12)–Ga(2)	106.05 (10)		

[a] $x, 1 + y, z$ symmetry transformation. [b] $x, -1 + y, z$ symmetry transformation. [c] $x, {}^1/_2 - y, z$ symmetry transformation. [d] $x, -{}^1/_2 - y, z$ symmetry transformation.

Cl(12) = 2.363 (3) and Ga(2)–Cl(12) = 2.369 (3) Å (average = 2.366 ± 0.004 Å); the Ga–C(mesityl) linkages are Ga(1)–C(11) = 1.970 (14) and Ga(2)–C(21) = 1.943 (12) Å (average = 1.957 ± 0.016 Å).

Each gallium(III) center has a rather distorted tetrahedral coordination environment. The smallest angles are those between the bridging chloride ligands [Cl(12)–Ga(1)–Cl(12) ($x, {}^1/_2 - y, z$) = 94.84 (9)° and Cl(12)–Ga(2)–Cl(12) ($x, -{}^1/_2 - y, z$) = 95.85 (9)°], and the largest are those between the terminal chloride and mesityl ligands [Cl(1)–Ga(1)–C(11) = 130.67 (34)° and Cl(2)–Ga(2)–C(21) = 133.56 (29)°]. Intermediate values are observed for Cl(terminal)–Ga–Cl(bridging) [99.58 (11)° and 99.02 (11)°] and Cl(bridging)–Ga–C(mesityl) bond angles [112.88 (34)° and 111.36 (28)°]. The Ga(1)–Cl(12)–Ga(2) angle is 106.05 (10)° as might be expected for a tetrahedral disposition of electron pairs about the bridging chloride ligand. All other distances and angles are in the normal range but of limited precision due to the rather poor quality of the crystals.

It is of interest to compare some average bond distances for $[GaMesCl_2]_\infty$ with those for $[Ga(C_5Me_5)Cl_2]_2$, the only other compound of the general formula $GaRCl_2$ to be investigated by an X-ray structural study.[11] No major differences were noted. For the compounds $[GaMesCl_2]_\infty$ and $[Ga(C_5Me_5)Cl_2]_2$, the average Ga–Cl(bridging) distances are 2.366 ± 0.004 and 2.362 ± 0.008 Å, whereas the average Ga–Cl(terminal) distances are 2.157 ± 0.010 and 2.124 ± 0.004 Å, respectively. The Ga–C(Mes) distance (1.957 ± 0.016 Å) is also similar to the $Ga–C(C_5Me_5)$ distance[11] (1.97 (1) Å).

The polymeric nature of $GaMesCl_2$ is likely to be responsible for its relatively high melting point, its insolubility in organic solvents, and its reactivity pattern with a strong base such as THF. A comparison of these properties of $GaMesCl_2$ with those for some related organogallium halides which are believed to be dimeric[18] suggests that $[GaMesCl_2)_\infty$ is unique in organogallium chemistry. It is noteworthy that a dimeric structure with bridging chloride atoms has been verified by X-ray structural studies for only two organogallium compounds,[11] $[Ga(C_5Me_5)_2Cl]_2$ and $[Ga(C_5Me_5)Cl_2]_2$, even though solution molecular weight and spectroscopic data are consistent with the proposed dimeric nature for a variety of other compounds.[18] A comparison of melting point and solubility data for compounds in the series GaR_3, GaR_2Cl, and $GaRCl_2$ (Table IV) suggest that only $GaMesCl_2$ has a unique polymeric structure. Only $GaMesCl_2$ among organogallium dihalides has a melting point which is significantly higher than the corresponding diorganogallium halide. Similarly, only $GaMesCl_2$ among the compounds listed in Table IV is insoluble in benzene, all others being soluble. It is also of interest to compare experimental observations when a base such as THF is added to organogallium halides mixed with benzene. The typical organogallium halide dissolved in benzene reacts rapidly with THF to form a solution of the simple 1:1 adduct. In contrast, when 0.136 mmol of $GaMesCl_2$ dispersed in benzene was combined with 0.0680 mmol of THF at room temperature, no apparent reaction occurred over 18 h. The off-white insoluble solid $GaMesCl_2$ remained. However, after the mixture was heated in a 70 °C oil bath for 15 min, all $GaMesCl_2$ dissolved and a clear solution formed. The ^1H NMR spectrum of this solution revealed typical sharp lines at δ 2.48 (ortho Me) and 2.04 (para Me) but broadened lines for THF. These observations suggest that an adduct with the stoichiometry of the reaction mixture $(GaMesCl_2)_2$·THF had formed. The most likely structure for this unique adduct would incorporate a small unit of the polymer and would have one bridging chloride atom, but all gallium atoms would be four-coordinate. It is unlikely that the solution contains a mixture of the 1:1 adduct (Cl_2MesGa·THF) and excess $GaMesCl_2$. For the 1:1 adduct to be formed, half of the available $GaMesCl_2$ would have to remain unreacted. The unreacted $GaMesCl_2$ would be expected to exist as a benzene-insoluble solid. If new soluble forms of $[GaMesCl_2]_n$ were present, exchange reactions with Cl_2MesGa·THF would be expected. It is of interest that our NMR spectra of $GaMes_2Cl$–THF and $–OEt_2$ solutions are also consistent with the formation of monochloride-bridged 2:1 adducts (see the following discussion). Monobridged 2:1 adducts have been previ-

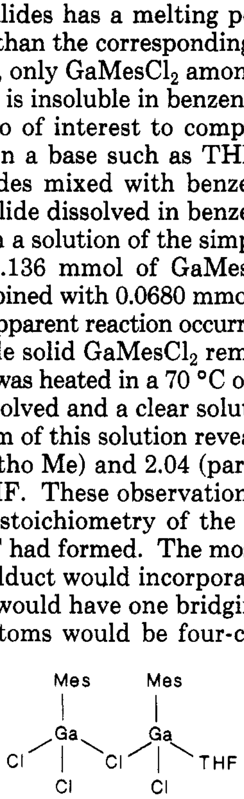

Table IV. Comparison of Melting Points (°C) of Aryl Gallium Compounds

	R (X)			
compd	Mes (Cl)	C_6H_5 (Cl)	C_6H_5 (Br)	C_6H_5 (I)
GaR_3	186–187.8[a]	166[b]	166[b]	166[b]
GaR_2X	158–1595	194–196[c]	223–225[c]	191–192[c]
$GaRX_2$	199–201.5	122–123[c]	134–135[c]	86–87[c]

[a] Reference 8. [b] Reference 19. [c] Reference 20.

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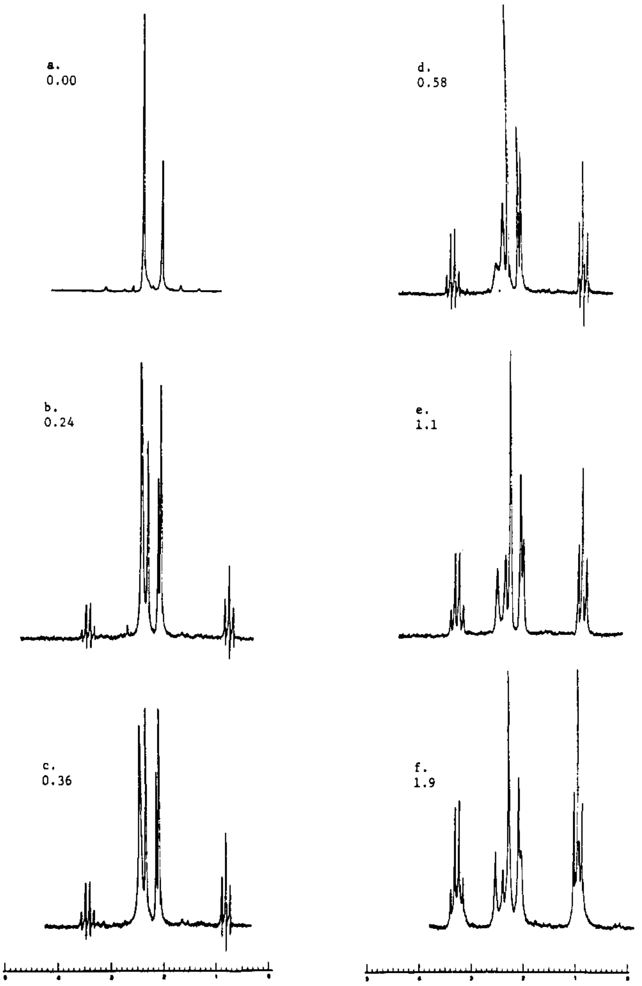
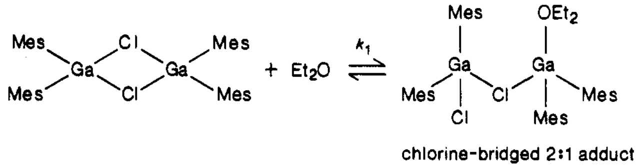


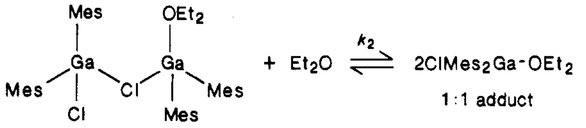
Figure 3. The 90-MHz ^{1}H NMR spectra (δ) of $GaMes_2Cl$ in benzene solution with increasing concentrations of diethyl ether given in millimoles of Et_2O/millimoles of $GaMes_2Cl$ (top left to bottom right).

ously described for some related aluminum[21,23] and gallium[22,23] compounds.

The ^{1}H NMR spectra (Figure 3) of solutions of $GaMes_2Cl$ and Et_2O in benzene are consistent with equilibria between the dimer, the monochloride-bridged 2:1 adduct, and the simple 1:1 adduct as shown by eq 3 and 4. A solution of the dimer $(GaMes_2Cl)_2$ in benzene with no added ether exhibited a ^{1}H NMR spectrum with two lines in the methyl region, 2.40 (ortho Me) and 2.07 (para Me) ppm (Figure 3a). After a small quantity of ether was added (0.24 mmol of Et_2O/mmol of $GaMes_2Cl$), four lines in the methyl region (2.44, 2.33, 2.14, and 2.07 ppm) were observed (Figure 3b). The predominate lines correspond to $(GaMes_2Cl)_2$. As the amount of ether was increased, the



(3)



(4)

lines at 2.33 and 2.14 ppm increased in intensity relative to those of the dimer (Figure 3c). The lines at 2.33 and 2.14 ppm are therefore assigned to ortho methyl and para methyl groups of the chloride-bridged 2:1 adduct. When the $Et_2O/GaMes_2Cl$ mole ratio was 0.58 or higher (Figure 3d–f), a new line at 2.57 ppm was evident and the relative integrations of the other four lines suggested that the line at 2.07 ppm arose from two components, the dimer and the 1:1 adduct. A high-resolution spectrum of $GaMes_2Cl$ with excess Et_2O in benzene revealed lines at 2.07 and 2.08 ppm in addition to the four other well-resolved lines in the methyl region. Consequently, the lines at 2.57 (ortho Me) and 2.08 (para Me) ppm are assigned to the 1:1 adduct. The three species shown in the two equilibria should exhibit six methyl lines, provided the mesityl groups in the chloride-bridged 2:1 adduct undergo rapid exchange. The number of observed lines and their intensities would eliminate the possibility of slow exchange for the chloride-bridged 2:1 adduct or the presence of an ionic species such as $Mes_2Ga(OEt_2)_2{}^+GaMes_2Cl_2{}^-$. It is noteworthy that when the $Et_2O/GaMes_2Cl$ mole ratio was 1.06 or higher, the species of highest concentration was the chloride-bridged 2:1 adduct. This conclusion suggests that chlorine is a better base than Et_2O in this system. When Et_2O and benzene were removed by vacuum distillation, both adducts dissociated at room temperature and the dimer was reformed. When the stronger base THF was utilized, $GaMes_2Cl$ formed an isolable 1:1 adduct. However, the ^{1}H NMR spectrum of a solution having a $GaMes_2Cl$/THF mole ratio of one exhibited a minimum of five lines in the methyl region. The multiple lines in the methyl region would be consistent with the existence of the two equilibria as previously described for the Et_2O system. The derivative with only one bulky mesityl group $GaMesCl_2$ also reacts with THF to form an isolable 1:1 adduct. However, the ^{1}H NMR spectrum reveals only two lines in the methyl region, δ 2.57 (ortho Me) and 2.11 (para Me), an observation consistent with the presence of only the 1:1 adduct.

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Registry No. $GaMeS_2Cl$, 109391-13-1; $GaMesCl_2$, 109391-14-2; $GaMes_3$, 60607-12-7; $GaCl_3$, 13450-90-3; $(GaMes_2Cl)_2$, 109391-15-3; $[(GaMes_2Cl)_2\cdot OEt_2]$, 109391-16-4.

Supplementary Material Available: A table of anisotropic thermal parameters (1 page); a list of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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