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Use of the 2,4,6-Tris(trifluoromethyl)phenyl Ligand in Organogallium Chemistry

Rodney D. Schluter, Harold S. Isom, Alan H. Cowley,* David A. Atwood,[1]
Richard A. Jones,* Falk Olbrich, Siegfried Corbelin, and Richard J. Lagow

Department of Chemistry and Biochemistry, The University of Texas at Austin,
Austin, Texas 78712

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The compounds $[R_FGa(\mu\text{-}Cl)Cl]_2$ (**1**), $[(R_F)_2Ga(\mu\text{-}Cl)]_2$ (**3**), and $(R_F)_3Ga$ (**4**) (R_F = 2,4,6-$(CF_3)_3C_6H_2$) have been prepared by treatment of the aryllithium reagent $[R_FLi{\cdot}Et_2O]_2$ with gallium trichloride. The hydroxy derivative $[R_FGa(\mu\text{-}OH)Cl]_2$ (**2**) was obtained as a hydrolysis product of **1**. All compounds have been characterzed by elemental analysis and multinuclear NMR and mass spectroscopy. X-ray crystallographic studies reveal that compound **1** adopts a chloride-bridged dimeric structure in which the gallium atoms are tetrahedrally coordinated and that **4** is monomeric and features a trigonal-planar geometry at gallium. X-ray analysis reveals a hydroxy-bridged dimeric structure for **2**. Single-crystal data are as follows: $[R_FGa(\mu\text{-}Cl)Cl]_2$ (**1**), orthorhombic, *Pbca*, with a = 9.569(2) Å, b = 16.787(1) Å, c = 16.608(3) Å, V = 2667.9(7) Å^3, Z = 4, and R = 0.0543 (R_w = 0.0602); $[R_FGa(\mu\text{-}OH)Cl]_2$ (**2**), triclinic, $P2_{1/n}$, with a = 8.063(1) Å, b = 18.335(3) Å, c = 24.234(3) Å, β = 90.21(1)°, V = 3582.6(8) Å^3, Z = 4, and R = 0.0521 (R_w = 0.114); $(R_F)_3Ga$ (**4**), triclinic, $P\bar{1}$, with a = 8.808(2) Å, b = 12.764(2) Å, c = 14.184(2) Å, α = 97.69(1)°, β = 95.19(1)°, γ = 106.46(1)°, V = 1501.5(4) Å^3, Z = 2, and R = 0.0434 (R_w = 0.0507). In general, it was found that the air stability and volatility of the new compounds increased with the degree of R_F substitution. Compounds **2** and **4** are stable to moist air.

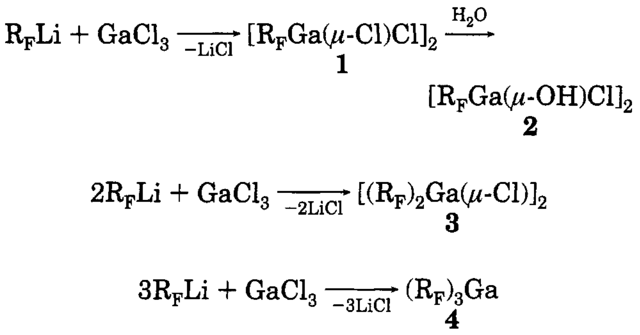
Introduction

The 2,4,6-tris(trifluoromethyl)phenyl ligand (R_F) has been shown to be capable of conferring stability on several unusual main-group compounds.[2] The special attributes of the R_F ligand include moderate steric bulk, a relatively high electron-withdrawing capability, and the possibility of short element–fluorine contacts involving the *o*-CF_3 groups. Interestingly, very little use of the R_F ligand has been made in the context of the group 13 elements. Apart from our communication on the synthesis and X-ray crystal structures of $(R_F)_2InIn(R_F)_2$ and $(R_F)_3In$,[3] other reports have been limited to the brief mention of R_FBCl_2, $(R_F)_2BCl$, and R_FGaCl_2 in a review article.[2] The present work is concerned with the details of the synthesis and characterization of mono-, di-, and trisubstituted R_F derivatives of gallium(III), namely $[R_FGa(\mu\text{-}Cl)Cl]_2$ (**1**), $[(R_F)_2Ga(\mu\text{-}Cl)]_2$ (**3**), and $(R_F)_3Ga$ (**4**). Single-crystal X-ray diffraction data are reported for **1** and **4**. The synthesis and X-ray crystal structure of the hydroxy derivative $[R_FGa(\mu\text{-}OH)Cl]_2$ (**2**) are also described.

Results and Discussion

Synthesis and Properties of Compounds 1–4. Compound **1** was synthesized in an overall yield of 24% via the salt elimination reaction of R_FLi with $GaCl_3$ in Et_2O solution at −78 °C (Scheme 1). The diethyl ether adduct $R_FGaCl_2{\cdot}Et_2O$ was isolated initially as an intermediate and converted into **1** by heating in vacuo at 75 °C. Hydrolysis of **1** with wet Et_2O resulted in formation of the chloro hydroxy dimer **2** in virtually quantitative yield. The bis- and tris-substituted R_F derivatives **3** and **4** were prepared in modest yields (32–35%) by treatment of $GaCl_3$ with 2 or 3 equiv of R_FLi, respectively, at −78 °C in Et_2O solution. On standing, solutions of **3** undergo a ligand redistribution reaction to **1** and **4**. Compounds **1** and **3** are hydrolytically sensitive. However, **2** and **4** are stable toward air and moisture. The inertness of **4** toward water contrasts with the typical hydrolytic sensitivity of trialkylgallium compounds.[4]

Scheme 1



$$R_FLi + GaCl_3 \xrightarrow[-LiCl]{} \underset{\mathbf{1}}{[R_FGa(\mu\text{-}Cl)Cl]_2} \xrightarrow{H_2O} \underset{\mathbf{2}}{[R_FGa(\mu\text{-}OH)Cl]_2}$$

$$2R_FLi + GaCl_3 \xrightarrow[-2LiCl]{} \underset{\mathbf{3}}{[(R_F)_2Ga(\mu\text{-}Cl)]_2}$$

$$3R_FLi + GaCl_3 \xrightarrow[-3LiCl]{} \underset{\mathbf{4}}{(R_F)_3Ga}$$

Characterization of Compounds 1–4. The dimeric nature of **1** in the gas phase was indicated by the observation of a peak at *m/z* 840 in the negative ion chemical ionization mass spectrum (CIMS), and the persistence of the dimer in the solid state was confirmed

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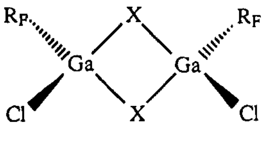
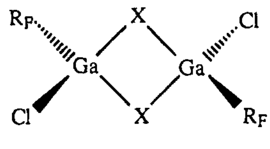
by X-ray crystallography (see later). For **2**, the presence of OH and R_F moieties in equal abundance was evident in the ^1H NMR spectrum, and OH stretching vibrations were detected in the IR spectrum at 3525 and 3675 cm^{-1}. A dimeric formulation for **2** was indicated by the observation of a CIMS peak at *m/z* 804; this formulation was confirmed by X-ray analysis. In the case of **3** it was not possible to obtain suitable crystals for study by X-ray diffraction. However, a dimeric chloride-bridged structure can be postulated on the basis of the observation of a CIMS peak at *m/z* 1332. The CIMS of **4** exhibits a cutoff at *m/z* 912 (M^-), thus implying that this compound is monomeric in the gas phase. X-ray analysis revealed the same molecularity in the solid state.

X-ray Crystal Structures of $[R_FGa(\mu\text{-}Cl)Cl]_2$ (1), $[R_FGa(\mu\text{-}OH)Cl]_2$ (2), and $(R_F)_3Ga$ (4). At the outset, it should be pointed out that there are two possible isomers for **1** and **2**, namely cis (**A**) and trans (**B**), which



A



B

X = Cl (**1**) or OH (**2**)

differ in the relative locations of the R_F and terminal Cl ligands. It was impossible to deduce the isomeric preference of **1** and **2** by spectroscopic means; hence, it was necessary to carry out X-ray diffraction studies. Interestingly, these studies revealed that **1** adopts structure **B** while **2** adopts structure **A**.

Compound **1** crystallizes in the orthorhombic space group *Pbca* with four molecules in the unit cell. There are no unusually short intermolecular contacts, and individual molecules of **1** reside on a C_2 axis. The molecular structure and atom-numbering scheme are illustrated in Figure 1, and selected metrical parameters have been assembled in Table 1. The dimeric molecules of **1** are held together by two chloride bridges, and the R_F and terminal chloride ligands adopt a mutually trans arrangement (isomer **B**). Such a structure presumably minimizes repulsions between the R_F moieties. The central Ga_2Cl_2 core is planar, and the intraannular angle at gallium (94.82(8)°) exceeds that at the chloride bridges (85.17(7)°). The opposite trend has been reported for $[t\text{-}BuGa(\mu\text{-}Cl)Cl]_2$, a compound with an overall structure similar to that of **1**.[5] The geometry at each gallium is approximately tetrahedral; however, there are considerable departures from the ideal bond angle, ranging from Cl(1)—Ga—Cl(1′) = 85.17(7)° to C(1)—Ga—Cl(2) = 123.4(2)°. The average terminal and bridging Ga—Cl bond lengths of 2.325(2) and 2.114(2) Å, respectively, are somewhat shorter than those reported for $[t\text{-}BuGa(\mu\text{-}Cl)Cl]_2$[5] and $[(2,4,6\text{-}(CH_3)_3C_6H_2)Ga(\mu\text{-}Cl)Cl]_\infty$.[6] This slight shrinkage effect may be a consequence of the electron-withdrawing nature of the R_F ligand.

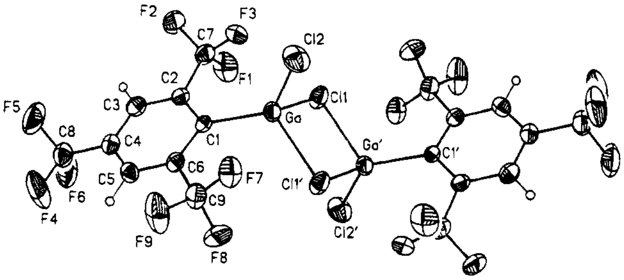


Figure 1. View of $[R_FGa(\mu\text{-}Cl)Cl]_2$ (1) showing the atom-labeling scheme. Thermal ellipsoids are scaled to the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[R_FGa(\mu\text{-}Cl)Cl]_2$ (1), $[R_FGa(\mu\text{-}OH)Cl]_2$ (2), and $(R_F)_3Ga$ (4)

Bond Lengths for Compound **1**			
Ga—Cl(1)	2.323(2)	Ga—Cl(1)′	2.328(2)
Ga—Cl(2)	2.114(2)	Ga—C(1)	1.976(6)
Bond Angles for Compound **1**			
Cl(1)—Ga—Cl(2)	106.19(9)	C(1)—Ga—Cl(1)	114.4(2)
Cl(2)—Ga—C(1)	123.4(2)	Ga′—Cl(1)—Ga	94.82(8)
Cl(1)′—Ga—Cl(1)	85.18(7)		
Bond Lengths for Compound **2**			
Ga(1)—Cl(1)	2.147(2)	Ga(2)—Cl(2)	2.143(2)
Ga(1)—C(1)	1.980(7)	Ga(2)—C(10)	1.979(6)
Ga(1)—O(1)	1.903(4)	Ga(2)—O(1)	1.895(4)
Ga(1)—O(2)	1.903(4)	Ga(2)—O(2)	1.892(5)
Bond Angles for Compound **2**			
Cl(1)—Ga(1)—O(1)	109.0(2)	Cl(2)—Ga(2)—O(1)	110.7(2)
Cl(1)—Ga(1)—O(2)	111.84(15)	Cl(2)—Ga(2)—O(2)	110.7(2)
O(1)—Ga(1)—O(2)	80.3(2)	O(1)—Ga(2)—O(2)	80.8(2)
O(1)—Ga(1)—C(1)	118.3(2)	O(1)—Ga(2)—C(10)	115.6(2)
O(2)—Ga(1)—C(1)	115.7(2)	O(2)—Ga(2)—C(10)	115.4(2)
C(1)—Ga(1)—Cl(1)	116.4(2)	C(10)—Ga(2)—Cl(2)	117.9(2)
Ga(1)—O(1)—Ga(2)	99.0(2)	Ga(1)—O(2)—Ga(2)	99.1(2)
Bond Lengths for Compound **4**			
Ga—C(11)	1.998(5)	Ga—C(21)	2.004(5)
Ga—C(31)	2.001(5)	Ga···F(171)	2.821
Ga···F(191)	2.783	Ga···F(271)	2.710
Ga···F(291)	2.775	Ga···F(371)	2.677
Ga···F(391)	2.683		
Bond Angles for Compound **4**			
C(11)—Ga—C(21)	121.8(2)	C(21)—Ga—C(31)	115.9(2)
C(11)—Ga—C(31)	122.3(2)		

Crystals of **2** belong to the monoclinic space group $P2_{1/n}$, and there are four molecules per unit cell. The molecular structure is illustrated in Figure 2 together with the atom-numbering protocol. Salient bond lengths and angles are assembled in Table 1. Like **1**, **2** exists as a dimer in the solid state and there are no significant intermolecular interactions. However, **2** is a hydroxide-bridged rather than chloride-bridged dimer, as expected on the basis of bond enthalpy considerations. The most interesting aspect of the structure is the fact that the dimer adopts the cis geometry (isomer **A**). The reason for the adoption of the sterically unfavored structure can be attributed to the fact that an Et_2O molecule is hydrogen-bonded to each of the bridging hydroxide groups. These Et_2O molecules are, however, weakly bound, because it was necessary to carry out the X-ray analysis at low temperature. Moreover, the Et_2O molecules were not detectable by NMR or IR spectroscopy. The steric interactions between the R_F moieties are manifested in the folding of the Ga_2O_2 ring by 9.0(2)°

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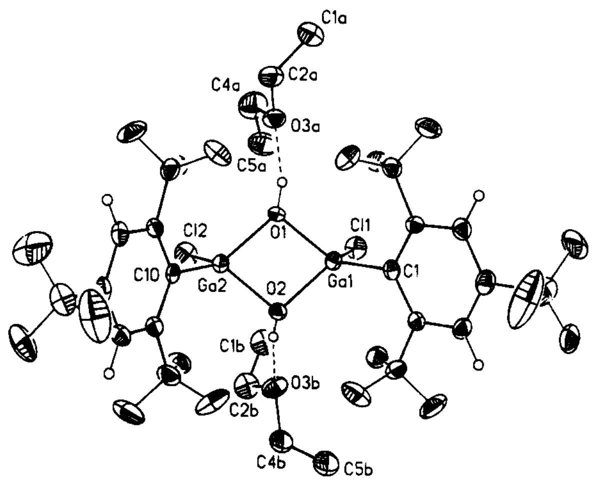

Figure 2. View of $[R_FGa(\mu\text{-}OH)Cl]_2$ (**2**) showing the atom-labeling scheme. Thermal ellipsoids are scaled to the 30% probability level.

along the O···O vector. As in other Ga_2O_2 ring systems such as $[(\eta^1\text{-}C_5H_5)_2Ga(\mu\text{-}OEt)]_2$ (**5**)[7] the Ga—O—Ga angle (99.0(2)°) is considerably larger than the O—Ga—O angle (80.3(2)°). The average Ga—O bond length for **2** (1.903)4) Å) is shorter than that in **5** (1.923(2) Å) or $[Ga(\mu\text{-}OH)Cl(C_{14}H_{17}N_3)]_2Cl_2{\cdot}H_2O$ (1.962 Å),[8] the only other chloro hydroxide complex of Ga of which we are aware. As in the case of **1**, this bond shortening is perhaps a consequence of the electronegativity of the R_F substituent. Although approximately tetrahedral, there is considerable variation in the bond angles at gallium, the smallest being O(1)—Ga(1)—O(2) = 80.3(2)° and the largest being C(1)—Ga(1)—Cl(1) = 116.4(2)°.

Compound **4** crystallizes in the triclinic space group $P\bar{1}$ as a monomer with two molecules in the unit cell. There are no short intermolecular contacts. A view of the molecule is shown in Figure 3, and important bond lengths and angles appear in Table 1. The structure is isomorphous with that of the analogous indium compound published previously.[3] Individual molecules of **4** possess approximate D_{3d} symmetry, and the GaC_3 geometry is trigonal planar. The R_F ligands are arranged in a propeller-like fashion around the gallium center with twist angles of 54.7° for the C(11) ligand, 47.4° for the C(21) ligand, and 47.0° for the C(31) ligand. This conformation places one o-CF_3 group above and one below the Ga atom in an overall trigonal-prismatic fashion. The Ga···F contacts in the secondary coordination sphere render the Ga atom nine-coordinate. Six intramolecular Ga···F contacts (one for each o-CF_3 group) fall in the range 2.665(19)–2.844(16) Å and are thus shorter than the sum of van der Waals radii (3.45 Å).[10] However, the average Ga···F contact of 2.740 Å is considerably longer than the sum of covalent radii (1.91 Å).[10] The average Ga—C bond length of 2.001(5) Å in **4** is slightly longer than in the unfluorinated tris(aryl) compounds $(Mes)_3Ga$ (1.968(4) Å)[9] and $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3Ga$ (1.972(11) Å),[11] presumably due to the larger steric demands of the R_F substituent.

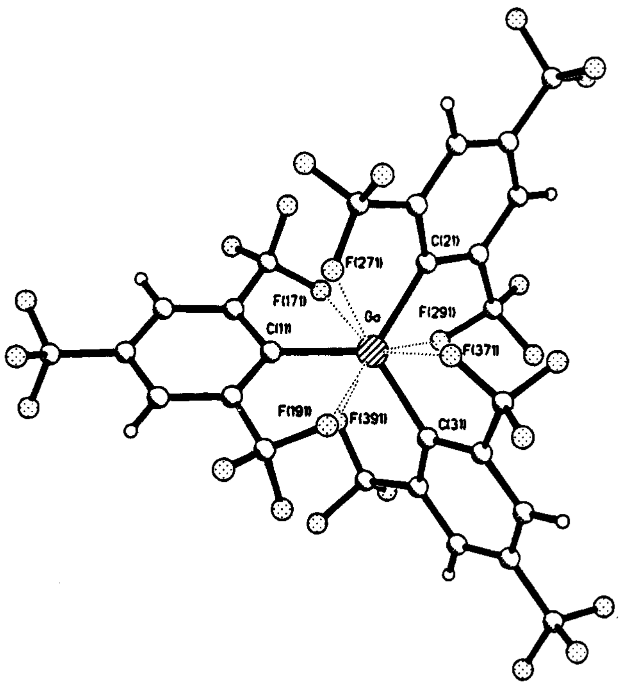

Figure 3. View of $(R_F)_3Ga$ (**4**) showing the atom-labeling scheme. Thermal ellipsoids are scaled to the 30% probability level.

NMR Spectra. Interactions between o-CF_3 fluorines and central atoms are manifested as observable ^{19}F–heteroatom coupling constants in the cases of R_F derivatives of phosphorus,[12] tin,[13] and lead.[14] For **4**, unsuccessful attempts were made to observe ^{19}F–^{71}Ga coupling constants. Nevertheless, the pattern of chemical shifts for the o- and p-CF_3 groups of **4** are very similar to those reported for the phosphorus, tin, and lead compounds.

In principle, it should be possible to detect the propeller-type rotation of the R_F groups of **4** by dynamic NMR. However, no changes were observed in the ^{19}F spectra in the range −80 to +30 °C.

Experimental Section

General Procedures. All manipulations were performed under dry, oxygen-free argon, under vacuum (using standard vacuum-line techniques), or in an argon-filled Vacuum Atmospheres drybox. Unless otherwise stated, all solvents were dried over sodium and distilled from sodium–benzophenone ketyl under argon prior to use. The reagents $GaCl_3$, 1,3,5-$(CF_3)_3C_6H_3$, and n-BuLi were procured commercially and used without further purification. The lithio derivative R_FLi was prepared according to the literature procedure.[15] Elemental analyses were performed by Atlantic Microlab, Inc.

Physical Measurements. IR spectra were obtained on a Digilab FTS-40 spectrometer. Mass spectra, EI and CI, were run on a Finnigan MAT 4023 instrument, and NMR spectra were run on a GE-300 spectrometer (^1H, 300.17 MHz; ^{13}C,

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Table 2. Crystallographic and Data Collection Parameters

compd	**1**	**2**	**4**
formula	$C_{18}H_4Cl_4F_{18}Ga_2$	$C_{26}H_{26}Cl_2F_{18}Ga_2O_4$	$C_{27}H_6F_{27}Ga$
fw	843.45	954.81	913.02
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Pbca*	$P2_1/n$	$P\bar{1}$
λ, Å	0.710 73	0.710 73	0.710 73
a, Å	9.569(2)	8.063(1)	8.808(2)
b, Å	16.787(1)	18.335(3)	12.764(2)
c, Å	16.608(3)	24.234(3)	14.184(2)
α, deg	90	90	97.69(1)
β, deg	90	90.21(1)	95.19(1)
γ, deg	90	90	106.46(1)
V, Å^3	2667.9(7)	3582.6(8)	1501.5(4)
Z	4	4	2
ϱ_{calc}, g cm^{-3}	2.11	1.77	2.019
μ_{calc}, cm^{-1}	25.63	17.71	11.06
no. of rflns	1500	5504	7521
no. of obs rflns	1343	4691	4850
R	0.0543	0.0521	0.0434
R_w[a]	0.0602	0.114	0.0507

[a] $R_w = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^4\}^{1/2}$, where the weight, w, is defined as follows: $w = 1/\{\sigma^2(|F_o|^2) + (0.0355P)^2 + 9.55P\}$; $P = [^1/_3(\text{maximum of 0 or } |F_o|^2) + {}^2/_3|F_o|^2]$.

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[R_FGa(\mu\text{-}Cl)Cl]_2$ (1)

atom	x/a	y/a	z/a	U_{eq}, Å^2
Ga	0.17888(8)	0.50084(5)	0.50189(5)	0.0468(3)
Cl(1)	0.0013(2)	0.57194(12)	0.43924(13)	0.0633(6)
Cl(2)	0.2667(3)	0.4266(2)	0.41237(13)	0.0870(10)
C(1)	0.2920(6)	0.5640(4)	0.5783(3)	0.039(2)
C(2)	0.3358(7)	0.6412(4)	0.5608(4)	0.045(2)
C(3)	0.4066(7)	0.6873(4)	0.6150(4)	0.051(2)
C(4)	0.4380(7)	0.6573(4)	0.6899(4)	0.046(2)
C(5)	0.4016(7)	0.5804(4)	0.7090(4)	0.048(2)
C(6)	0.3325(7)	0.5348(4)	0.6540(4)	0.043(2)
C(7)	0.3097(10)	0.6783(6)	0.4786(5)	0.069(3)
F(1)	0.1941(7)	0.7209(3)	0.4779(4)	0.100(3)
F(2)	0.4145(7)	0.7249(4)	0.4580(3)	0.119(3)
F(3)	0.2976(5)	0.6232(3)	0.4215(3)	0.078(2)
C(8)	0.5137(10)	0.7072(5)	0.7492(6)	0.069(3)
F(4)	0.5490(9)	0.6712(4)	0.8156(4)	0.139(4)
F(5)	0.6287(7)	0.7381(5)	0.7215(4)	0.153(3)
F(6)	0.4407(7)	0.7682(4)	0.7746(4)	0.127(3)
C(9)	0.2968(9)	0.4499(4)	0.6782(5)	0.065(3)
F(7)	0.2883(5)	0.4010(2)	0.6158(3)	0.074(2)
F(8)	0.1789(6)	0.4441(3)	0.7172(3)	0.100(3)
F(9)	0.3957(7)	0.4216(3)	0.7274(4)	0.127(3)

75.48 MHz; ^{19}F, 282.36 MHz). NMR spectra are referenced to C_6D_6, which was dried over 4-Å sieves and distilled prior to use; ^1H and ^{13}C chemical shifts are reported relative to $Si(CH_3)_4$ (0.00 ppm), and ^{19}F chemical shifts are referenced to $CFCl_3$ (0.00 ppm). Melting points were obtained in sealed capillaries under argon (1 atm) and are uncorrected.

Synthesis of $[(2,4,6\text{-}(CF_3)_3C_6H_2)Ga(\mu\text{-}Cl)Cl]_2$ (1). A solution of 17.7 mmol of R_FLi in 30 mL of Et_2O was cooled to −78 °C and added via cannula to a solution of 3.12 g (17.7 mmol) of $GaCl_3$ in 30 mL of Et_2O at −78 °C. The stirred reaction mixture was warmed slowly to 25 °C overnight. A beige solution and a white precipitate resulted. Removal of the solvent resulted in a dark-colored oil, which upon distillation at 75 °C (10 mTorr) produced 5.55 g (11.2 mmol, 63.3% yield) of a clear oil (extrapolated bp 310−320 °C). ^1H NMR (C_6D_6): δ 7.78 (s, 2H, *m*-H), 3.96 (q, 4H, $O(CH_2CH_3)_2$), 1.05 (t, 6H, $O(CH_2CH_3)_2$). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 138.44 (q, $^2J_{CF} = 32.0$ Hz, *o* aryl C), 132.52 (q, $^2J_{CF} = 34.5$ Hz, *p* aryl C), 126.25 (s, *m* aryl C), 125.73 (s, *ipso*-C), 123.30 (q, $^1J_{CF} = 274.6$ Hz, *o*-CF_3), 122.36 (q, $^1J_{CF} = 272.9$ Hz, *p*-CF_3). MS (EI): *m/z* 385 ($M^+ - Cl - Et_2O$). The clear oil (4.6 g, 9.3 mmol) was placed in a 100-mL round-bottom flask equipped with a reflux condenser, heated to reflux at 75 °C (10 mTorr) for 1 h, and then cooled while still under vacuum. Colorless crystals of **1** sublimed into the reflux condenser. The reflux condenser was transferred to an empty 100-mL round-bottom flask, and toluene was used to wash the crystals into the flask. Removal of the solvent afforded 1.48 g (1.77 mmol, 38% yield) of **1** as a colorless solid: mp 146−148 °C. ^1H NMR (C_6D_6): δ 8.10 (s, *m*-H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.03 (q, $^2J_{CF} = 31.8$ Hz, *o* aryl C), 132.99 (q, $^2J_{CF} = 34.3$ Hz, *p* aryl C), 126.51 (s, *m* aryl C), 125.93 (s, *ipso*-C), 123.94 (q, $^1J_{CF} = 275.0$ Hz, *o*-CF_3), 123.03 (q, $^1J_{CF} = 272.7$ Hz, *p*-CF_3). ^{19}F NMR (THF-d_8): δ −57.98 (s, 3F, *o*-CF_3), −59.83 (s, 3F, *o*-CF_3), −64.16 (s, 3F, *p*-CF_3). MS (CI): *m/z* 420 ($M^-/2$). Anal. Calcd for $C_9H_2Cl_2F_9Ga$: C, 25.63; H, 0.48. Found: C, 26.16; H, 1.04.

Synthesis of $[(2,4,6\text{-}(CF_3)_3C_6H_2)Ga(\mu\text{-}OH)Cl]_2$ (2). An excess of wet Et_2O was added to 0.5 g (0.6 mmol) of **1** in 5 mL of Et_2O at 25 °C. A reaction occurred immediately, as evidenced by the formation of gas bubbles. The solvent and volatiles were removed under reduced pressure, and the resulting white powder was recrystallized from the minimum amount of Et_2O. Storage of the solution overnight at −20 °C resulted in a virtually quantitative yield of colorless crystalline **2**: mp 169−171 °C. ^1H NMR (C_6D_6): δ 7.46 (s, 4H, aryl *H*), 0.29 (s, 2H, O*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.90 (q, $^2J_{CF} = 32.0$ Hz, *o* aryl C), 133.27 (q, $^2J_{CF} = 34.6$ Hz, *p* aryl C), 126.85 (s, *m* aryl C), 125.81 (s, *ipso*-C), 123.91 (q, $^1J_{CF} = 275.6$ Hz, *o*-CF_3), 122.42 (q, $^1J_{CF} = 273.2$ Hz, *p*-CF_3). ^{19}F NMR (C_6D_6): δ −59.41 (s, 6F, *o*-CF_3), −63.82 (s, 3F, *p*-CF_3). MS (CI): *m/z* 804 (M^+). IR (KBr): ν(OH) 3675 (vs), 3525 (br) cm^{-1}. Anal. Calcd for $C_{18}H_6F_{18}Cl_2Ga_2O_2$: C, 26.81; H, 0.75. Found: C, 27.22; H, 1.20. Compound **3** is stable to air and moisture in the solid state.

Synthesis of $[(2,4,6\text{-}(CF_3)_3C_6H_2)_2Ga(\mu\text{-}Cl)]_2$ (3). A solution of 20.8 mmol of R_FLi in 30 mL of Et_2O was added via cannula to 1.85 g (10.4 mmol) of $GaCl_3$ in 30 mL of Et_2O at −78 °C. The stirred reaction mixture was warmed to room temperature overnight, resulting in the formation of a white precipitate (LiCl) and a pale yellow solution. The reaction mixture was filtered, and the filtate was concentrated to a volume of 5 mL. A few drops of benzene were added to help induce crystallization. Cooling the resulting solution overnight to −20 °C resulted in 2.21 g (3.3 mmol, 32% yield) of **3** as a pale yellow powder: mp 69−71 °C. ^1H NMR (C_6D_6): δ 8.39 (s, 8H, *m-H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.08 (q, $^2J_{CF} = 35.8$ Hz, *o* aryl C), 133.69 (q, $^2J_{CF} = 34.5$ Hz, *p* aryl C), 126.99 (s, *m* aryl C), 122.07 (s, *ipso*-C), 124.90 (q, $^1J_{CF} = 274.9$ Hz, *o*-CF_3), 123.95 (q, $^1J_{CF} = 272.0$ Hz, *p*-CF_3). ^{19}F NMR (THF/C_6D_6): δ −57.84 (s, 24F, *o*-CF_3), −63.90 (s, 12F, *p*-CF_3). MS (CI): *m/z* 1332 (M^-). Anal. Calcd for $C_{18}H_4F_{18}GaCl$: C, 32.40; H, 0.60. Found: C, 32.03; H, 0.78.

Synthesis of $(2,4,6\text{-}(CF_3)_3C_6H_2)_3Ga$ (4). A solution of 22.4 mmol of R_FLi in 30 mL of Et_2O was added to 1.3 g (7.4 mmol) of $GaCl_3$ dissolved in 30 mL of Et_2O and cooled to −78 °C. The reaction mixture was warmed to room temperature overnight, resulting in a fine white powder (LiCl) and a yellow solution. The reaction mixture was filtered, and the filtrate was concentrated to a volume of 30 mL. Cooling the solution to −20 °C overnight afforded 2.4 g (2.6 mmol, 35% yield) of **4** as a pale yellow powder. Further purification of **4** was achieved via sublimation at 70 °C (0.01 Torr): mp 180 °C. ^1H NMR (THF, C_6D_6): δ 8.84 (s, 6H, *m-H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.22 (q, $^2J_{CF} = 35.8$ Hz, *o* aryl C), 133.71 (q, $^2J_{CF} = 34.5$ Hz, *p* aryl C), 127.02 (s, *m* aryl C), 125.73 (s, *ipso*-C), 125.05 (q, $^1J_{CF} = 275.1$ Hz, *o*-CF_3), 123.98 (q, $^1J_{CF} = 271.9$ Hz, *p*-CF_3). ^{19}F NMR (THF, C_6D_6): δ −63.97 (s, 9F, *p*-CF_3), −58.42 (s, 18F, *o*-CF_3). MS (CI): *m/z* 912 (M^-). HRMS (CI): *m/z* calcd for $C_{27}H_6F_{27}Ga$ 911.9294, found 911.9283 (M^-). Anal. Calcd for $C_{27}H_6F_{27}Ga$: C, 35.52; H, 0.66. Found: C, 35.15; H, 0.81.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **1**, **2**, and **4** are given in Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters for **1**, **2**, and **4** are presented in Tables 3−5, respectively. The crystals were

Table 4. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[R_FGa(\mu\text{-}OH)Cl]_2$ (2)

atom	*x*/*a*	*y*/*a*	*z*/*a*	U_{eq}, Å^2
Ga(1)	0.00980(9)	0.27109(4)	0.89825(3)	0.0324(3)
Ga(2)	0.02588(9)	0.31855(4)	0.78481(3)	0.0325(3)
Cl(1)	0.2335(2)	0.29389(11)	0.94338(8)	0.0508(7)
Cl(2)	0.2609(2)	0.36499(13)	0.76342(9)	0.0590(8)
O(1)	−0.0458(6)	0.3536(2)	0.8543(2)	0.032(2)
O(2)	0.0549(6)	0.2326(3)	0.8269(2)	0.035(2)
C(1)	−0.1697(8)	0.2221(4)	0.9397(3)	0.032(2)
C(2)	−0.1787(9)	0.1460(4)	0.9450(3)	0.036(3)
C(3)	−0.3002(10)	0.1120(4)	0.9760(3)	0.044(3)
C(4)	−0.4184(9)	0.1531(4)	1.0034(3)	0.045(3)
C(5)	−0.4138(9)	0.2280(4)	1.0003(3)	0.040(3)
C(6)	−0.2921(8)	0.2614(4)	0.9683(3)	0.031(2)
C(7)	−0.0548(11)	0.0981(4)	0.9168(4)	0.052(3)
F(7A)	0.0940(5)	0.1288(2)	0.9133(2)	0.054(2)
F(7B)	−0.0350(7)	0.0350(3)	0.9419(3)	0.098(3)
F(7C)	−0.1008(7)	0.0833(3)	0.8650(2)	0.081(2)
C(9)	−0.2978(9)	0.3429(4)	0.9661(3)	0.042(3)
F(9A)	−0.3688(5)	0.3678(2)	0.9204(2)	0.057(2)
F(9B)	−0.3786(6)	0.3721(3)	1.0084(2)	0.069(2)
F(9C)	−0.1431(5)	0.3714(2)	0.9675(2)	0.047(2)
C(10)	−0.1470(8)	0.3133(4)	0.7268(3)	0.030(2)
C(11)	−0.1625(9)	0.2531(4)	0.6911(3)	0.039(3)
C(12)	−0.2902(10)	0.2476(4)	0.6530(3)	0.045(3)
C(13)	−0.4059(9)	0.3016(4)	0.6481(3)	0.040(3)
C(14)	−0.3924(9)	0.3631(4)	0.6805(3)	0.041(3)
C(15)	−0.2644(9)	0.3677(4)	0.7194(3)	0.034(2)
C(16)	−0.0413(11)	0.1919(5)	0.6928(3)	0.056(3)
F(16A)	−0.0917(7)	0.1367(3)	0.7242(3)	0.092(2)
F(16B)	−0.0132(7)	0.1646(3)	0.6426(2)	0.094(2)
F(16C)	0.1074(6)	0.2115(2)	0.7122(2)	0.058(2)
C(18)	−0.2629(10)	0.4362(4)	0.7533(3)	0.043(3)
F(18A)	−0.1075(5)	0.4547(2)	0.7688(2)	0.046(2)
F(18B)	−0.3480(5)	0.4288(3)	0.7997(2)	0.064(2)
F(18C)	−0.3242(7)	0.4933(3)	0.7270(2)	0.088(2)
C(1A)	−0.1804(12)	0.5667(5)	0.9446(3)	0.079(4)
C(2A)	−0.1477(12)	0.5299(5)	0.8923(4)	0.070(4)
O(3A)	0.0074(7)	0.4893(3)	0.8909(2)	0.053(2)
C(4A)	0.1482(13)	0.5332(6)	0.8834(5)	0.089(5)
C(5A)	0.2997(12)	0.4901(5)	0.8889(4)	0.085(4)
C(1B)	0.534(2)	0.2240(10)	0.8266(7)	0.085(5)
C(2B)	0.469(2)	0.1671(9)	0.7885(7)	0.078(4)
C(2BA)	0.472(4)	0.177(2)	0.8363(13)	0.078(4)
C(1BA)	0.588(4)	0.195(2)	0.8001(14)	0.085(5)
O(3B)	0.3096(6)	0.1449(3)	0.8097(2)	0.061(2)
C(4B)	0.2860(13)	0.0686(5)	0.7956(4)	0.076(4)
C(5B)	0.3549(15)	0.0193(6)	0.8374(4)	0.100(5)
C(17)	−0.5447(5)	0.2948(3)	0.6062(2)	0.064(4)
F(17A)	−0.4962(12)	0.2634(10)	0.5595(3)	0.089(4)
F(17B)	−0.611(2)	0.3591(4)	0.5933(7)	0.121(5)
F(17C)	−0.666(2)	0.2539(11)	0.6266(4)	0.122(6)
F(17D)	−0.6825(15)	0.326(2)	0.6244(7)	0.089(4)
F(17E)	−0.580(3)	0.2261(3)	0.5928(10)	0.121(5)
F(17F)	−0.496(2)	0.328(2)	0.5604(6)	0.122(6)
C(8)	−0.5524(5)	0.1124(3)	1.0392(2)	0.075(4)
F(8A)	−0.615(2)	0.0548(8)	1.0130(6)	0.145(6)
F(8B)	−0.674(2)	0.1612(8)	1.0399(9)	0.071(3)
F(8C)	−0.497(2)	0.1013(12)	1.0903(3)	0.148(6)
F(8D)	−0.6844(8)	0.1047(6)	1.0066(4)	0.148(6)
F(8E)	−0.4960(8)	0.0473(3)	1.0545(3)	0.071(3)
F(8F)	−0.5799(14)	0.1534(3)	1.0835(4)	0.145(6)

Table 5. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $(R_F)_3Ga$ (4)

atom	*x*/*a*	*y*/*a*	*z*/*a*	U_{eq}, Å^2
Ga	0.0810(1)	0.2182(1)	0.2786(1)	0.021(1)
C(11)	0.2632(4)	0.2166(3)	0.3726(2)	0.022(1)
C(12)	0.3549(4)	0.1435(3)	0.3561(2)	0.022(1)
C(13)	0.4788(4)	0.1405(3)	0.4224(2)	0.024(1)
C(14)	0.5185(4)	0.2135(3)	0.5084(2)	0.025(1)
C(15)	0.4348(4)	0.2880(3)	0.5274(2)	0.028(1)
C(16)	0.3083(4)	0.2887(3)	0.4618(2)	0.026(1)
C(17)	0.3184(4)	0.0615(3)	0.2640(2)	0.025(1)
F(171)	0.2770(3)	0.1066(2)	0.1883(1)	0.035(1)
F(172)	0.1956(3)	−0.0276(2)	0.2651(2)	0.038(1)
F(173)	0.4420(3)	0.0262(2)	0.2435(2)	0.043(1)
C(18)	0.6539(5)	0.2145(3)	0.5804(3)	0.036(1)
F(181)	0.6172(4)	0.2217(3)	0.6685(2)	0.082(2)
F(182)	0.7011(5)	0.1256(3)	0.5642(2)	0.088(2)
F(183)	0.7811(4)	0.2994(3)	0.5828(3)	0.087(2)
C(19)	0.2247(5)	0.3720(3)	0.4897(3)	0.035(1)
F(191)	0.0676(3)	0.3363(2)	0.4558(2)	0.043(1)
F(192)	0.2812(4)	0.4657(2)	0.4548(2)	0.063(1)
F(193)	0.2341(4)	0.3998(3)	0.5840(2)	0.074(1)
C(21)	−0.0037(4)	0.0782(3)	0.2123(2)	0.022(1)
C(22)	−0.1631(4)	−0.0059(3)	0.2609(3)	0.025(1)
C(23)	−0.2821(4)	−0.0999(3)	0.2148(3)	0.029(1)
C(24)	−0.2573(4)	−0.1123(3)	0.1176(3)	0.033(1)
C(25)	−0.3305(4)	−0.0330(3)	0.067(3)	0.032(1)
C(26)	−0.1361(4)	0.0600(3)	0.1132(3)	0.026(1)
C(27)	−0.1245(5)	−0.0009(3)	0.3673(3)	0.030(1)
F(271)	−0.0448(3)	0.1009(2)	0.4136(2)	0.042(1)
F(272)	−0.2581(3)	−0.0314(2)	0.4083(2)	0.052(1)
F(273)	−0.0415(4)	−0.0670(3)	0.3885(2)	0.068(1)
C(28)	−0.4633(6)	−0.2127(4)	0.0679(4)	0.051(2)
F(281)	−0.4802(8)	−0.2273(5)	−0.0224(3)	0.122(3)
F(282)	−0.6004(5)	−0.2111(5)	0.0951(5)	0.117(3)
F(283)	−0.4511(9)	−0.3061(4)	0.0968(7)	0.164(4)
F(1*)	−0.4055(18)	−0.2749(13)	0.0133(12)	0.046(3)
F(2*)	−0.5222(23)	−0.2706(15)	0.0172(12)	0.053(4)
F(3*)	−0.5640(25)	−0.1757(16)	0.0176(17)	0.081(5)
C(29)	−0.0632(5)	0.1445(3)	0.0520(3)	0.029(1)
F(291)	0.0930(3)	0.1944(2)	0.0823(2)	0.036(1)
F(292)	−0.0737(3)	0.0992(2)	−0.0394(2)	0.043(1)
F(293)	−0.0328(3)	0.2248(2)	0.0538(2)	0.042(1)
C(31)	0.0491(4)	0.3592(3)	0.2467(2)	0.022(1)
C(32)	−0.0956(4)	0.3833(3)	0.2545(2)	0.025(1)
C(33)	−0.1249(5)	0.4777(3)	0.2279(3)	0.032(1)
C(34)	−0.0066	0.5532(3)	0.1939(3)	0.033(1)
C(35)	0.1395(5)	0.5350(3)	0.1855(3)	0.033(1)
C(36)	0.1654(4)	0.4397(3)	0.2122(3)	0.025(1)
C(37)	−0.2358(4)	0.3060(3)	0.2886(3)	0.032(1)
F(371)	−0.1934(3)	0.2337(2)	0.3375(2)	0.036(1)
F(372)	−0.3121(4)	0.3585(2)	0.3447(3)	0.065(1)
F(373)	−0.3435(3)	0.2443(3)	0.2153(2)	0.062(1)
C(38)	−0.0374(6)	0.6553(4)	0.1649(4)	0.051(2)
F(381)	−0.1275(8)	0.6940(4)	0.2188(4)	0.146(4)
F(382)	0.0923(5)	0.7369(3)	0.1696(3)	0.101(2)
F(383)	−0.0989(6)	0.6385(3)	0.0751(3)	0.107(2)
F(4*)	−0.1812(31)	0.6449(21)	0.1505(20)	0.037(6)
C(39)	0.3289(5)	0.4302(3)	0.2020(3)	0.034(1)
F(391)	0.3414(3)	0.3287(2)	0.2084(2)	0.039(1)
F(392)	0.3746(4)	0.4515(3)	0.1183(2)	0.067(1)
F(393)	0.4397(3)	0.5001(3)	0.2675(3)	0.081(1)

mounted in thin-walled glass capillaries and sealed under argon.

$[(2,4,6\text{-}(CF_3)_3C_6H_2)Ga(\mu\text{-}Cl)Cl]_2$ (1). Colorless crystals of 1 suitable for X-ray diffraction study were grown by sublimation at 75 °C (10 mTorr). The data for 1 were collected at 298 K on an Enraf-Nonius CAD-4 diffractometer with a 2θ range between 2.0 and 45.0° using graphite-monochromated Mo Kα radiation. Three standard reflections were measured every 97 reflections to monitor instrument and crystal stability. The structure was solved by direct methods and refined using full-matrix least squares. All calculations were performed using SHELXA software.[16]

$[(2,4,6\text{-}(CF_3)_3C_6H_2)Ga(\mu\text{-}OH)Cl]_2$ (2). The data were collected at 173 K on a Nicolet P3 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using graphite-monochromated Mo Kα radiation. Four reflections were remeasured every 96 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The scaling factor ranged from 0.991 to 1.01. The data were corrected for Lorentz and polarization effects. An absorption correction was applied based on differences in observed and calculated structure factors using the routine SHELXA.[16] Data reduction and

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(16) Sheldrick, G. M. SHELXA: A Computer Program to Estimate Systemic Errors in the Data by Differences in the Observed and Calculated Structure Factor Amplitudes; 1993.

decay correction were performed using the SHELXTL-*Plus* software package.[17] The structure was solved by direct methods and refined on F^2 by full-matrix least squares[18] with anisotropic thermal parameters for all non-H atoms, except for the atoms of the trifluoromethyl groups (C(8), F(8A–F) and C(17), F(17A–F)) *para* to the Ga atoms and one ethyl group (C(1B), C(2B)) on an Et_2O molecule. The hydrogen atoms were calculated in idealized positions (C—H = 0.96 Å) with isotropic temperature factors set to $1.2U_{eq}$ of the relevant atom. The CF_3 groups were refined by fixing the C—F bonds to equal 1.33 Å. The structure was refined on F_o^2 using SHELXL93.[18] The function $\Sigma_w(|F_o|^2 - |F_c|^2)^2$ was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.184P)^2 + (0.412P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$.

(2,4,6-(CF_3)$_3$$C_6H_2$)$_3$Ga (4). The data were collected at 163 K on a Siemens P4 diffractometer, equipped with a Siemens LT-2A low-temperature device and using graphite-monochromated Mo Kα radiation. Three standard reflections were measured every 97 reflections to monitor instrument and crystal stability. All calculations were performed using the SHELXTL-*Plus* software package.[17] No absorption correction was applied. The structure was solved by Patterson methods and refined by using full-matrix least squares with anisotropic thermal parameters for all non-H atoms. The hydrogen atoms were located from the Fourier differential map and, together with the isotropic temperature factor, refined in subsequent least squares. Disorder was found in the *p*-CF_3 groups, and a disorder model was applied.

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Supplementary Material Available: Tables of bond lengths, bond angles, H atom atomic coordinates, and thermal parameters for **1**, **2**, and **4** (20 pages). Ordering information is given on any current masthead page.

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