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Monomeric Gallium(III) Compounds Containing Three Different Ligands. Crystal and Molecular Structures of GaMeCl(acac) and GaCl[N(SiMe$_3$)$_2$](acac)

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Five monomeric gallium(III) compounds, each containing three different ligands, have been prepared by metathetical and/or ligand redistribution reactions and identified as single compounds in benzene solution and in the solid phase, as appropriate. These compounds include GaRCl(acac) (R = Me, Et, Mes (mesityl, $C_6H_2Me_3$); acac = 2,4-pentanedionato), GaCl[N(SiMe$_3$)$_2$](acac), and GaMe[N(SiMe$_3$)$_2$](acac). X-ray structural studies of GaMeCl(acac) and GaCl[N(SiMe$_3$)$_2$](acac) confirmed the presence of the three different ligands bonded to gallium in these monomeric molecules. The related derivatives GaMeCl(hfac) and GaMesCl(hfac) (hfac = 1,1,1,5,5,5-hexafluoropentanedionato) were also prepared and characterized, but these compounds slowly decomposed at room temperature.

Introduction

Group 13 compounds that incorporate different ligands may undergo ligand redistribution reactions to form an equilibrium with multiple symmetrized species. Consequently, chemically stable, fully characterized, pure monomeric compounds with two and three different ligands are unusual. The heteroleptic organogallium(III) compounds $R_{3-n}GaCp_n$ (R = Me,[1,2] Et;[2,3] Cp = C_5H_5,[1,3] C_5H_4Me;[2] $n = 1, 2$) underwent ligand redistribution reactions to form equilibrium mixtures of GaR_3, $R_2Ga(C_5H_5)$, $RGa(C_5H_5)_2$, and $Ga(C_5H_5)_3$, when they dissolved either in benzene or in THF, a strong Lewis base. It was, however, unusual that these compounds were isolated in very high yields as pure crystalline solids. The uninegative, bidentate β-diketonato ligand (bdk) appears to enhance the stability of the group 13 compounds[4,5] into which it is incorporated. Thus, this type of ligand might reduce the tendency of compounds to undergo ligand redistribution reactions and permit the isolation of monomeric derivatives with three different ligands GaXY(bdk). In the following paper, the 2,4-pentanedionato ligand (acac) has been shown to be effective at stabilizing gallium(III) compounds with three different ligands GaXY(acac) both in the solid state and in solution. In contrast, analogous compounds with the 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfac) ligand were unstable and underwent ligand redistribution reactions to form $Ga(hfac)_3$.

Results and Discussion

Five monomeric gallium compounds with three different ligands, GaRCl(acac) (R = Me, Et, Mes), GaCl[N(SiMe$_3$)$_2$](acac) and GaMe[N(SiMe$_3$)$_2$](acac), have been prepared by metathetical and/or ligand redistribution reactions and identified as single compounds. All three compounds of the type GaRCl(acac) were prepared in excellent yields by using stoichiometric quantities of reagents in metathetical reactions (eq 1). The derivatives GaMeCl(acac) and GaMesCl(acac) were also prepared by stoichiometric ligand redistribution reactions (eq 2) at room temperature. The reaction between GaMe$_2$(acac) and GaCl$_2$(acac) was faster than the reaction between GaMes$_2$(acac) and GaCl$_2$(acac). The other two unsymmetrically substituted compounds GaX[N(SiMe$_3$)$_2$](acac) (X = Me, Cl) were prepared by metathetical reactions between either GaCl$_2$(acac) or GaMeCl(acac) and LiN(SiMe$_3$)$_2$·OEt$_2$, as appropriate (eq 3).

$$^{1}/_{2}(\mathrm{GaRCl_2})_2 + \mathrm{Na(acac)} \xrightarrow[20\ °\mathrm{C}]{\text{benzene}} \mathrm{GaRCl(acac)} + \mathrm{NaCl_{(s)}} \tag{1}$$

$$\mathrm{GaCl_2(acac)} + \mathrm{GaR_2(acac)} \xrightarrow{\mathrm{R = Me,\ Mes}} 2\mathrm{GaRCl(acac)} \tag{2}$$

$$\mathrm{GaMeCl(acac)} + \mathrm{LiN(SiMe_3)_2} \xrightarrow{\text{diethyl ether}} \mathrm{GaMe[N(SiMe_3)_2](acac)} + \mathrm{LiCl_{(s)}} \tag{3}$$

The physical properties, elemental analyses, cryoscopic molecular weights, and NMR spectra are consistent with GaRCl(acac) (R = Me, Et, Mes), Ga(Me)[N(SiMe$_3$)$_2$](acac), and Ga(Cl)[N(SiMe$_3$)$_2$](acac) being pure, single, monomeric species with four-coordinate gallium centers in all phases studied. Two of the compounds, GaRCl(acac) (R = Me, Mes), were solids at

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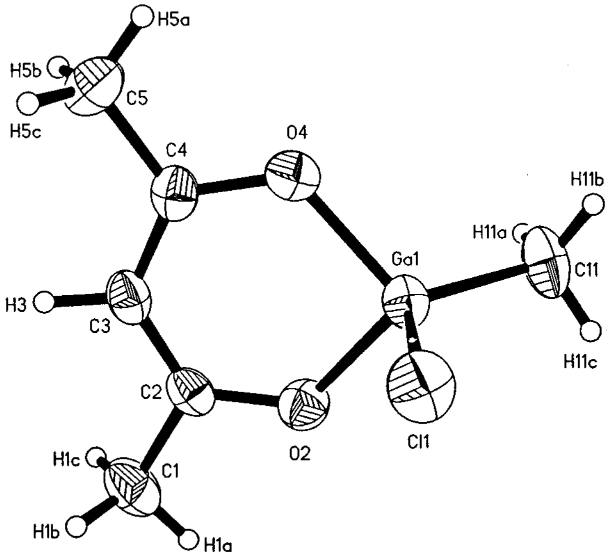

Figure 1. Molecular geometry and labeling of atoms for GaMeCl(acac) (30% probability ellipsoids for non-hydrogen atoms, hydrogen atoms artifically reduced).

Table 1. Selected Bond Distances (Å) and Angles (deg) for GaMeCl(acac)

(A) Gallium−Ligand Distances			
Ga(1)−Cl(1)	2.181(4)	Ga(1)−O(2)	1.901(7)
Ga(1)−C(11)	1.925(12)	Ga(1)−O(4)	1.878(7)
(B) Distances within the acac Chelate Ring			
O(2)−C(2)	1.309(11)	O(4)−C(4)	1.318(11)
C(2)−C(3)	1.372(15)	C(3)−C(4)	1.372(14)
(C) Angles around Gallium			
Cl(1)−Ga(1)−O(2)	103.5(3)	O(2)−Ga(1)−O(4)	96.3(3)
Cl(1)−Ga(1)−O(4)	103.4(3)	O(2)−Ga(1)−C(11)	116.0(5)
Cl(1)−Ga(1)−C(11)	118.6(5)	O(4)−Ga(1)−C(11)	115.8(5)

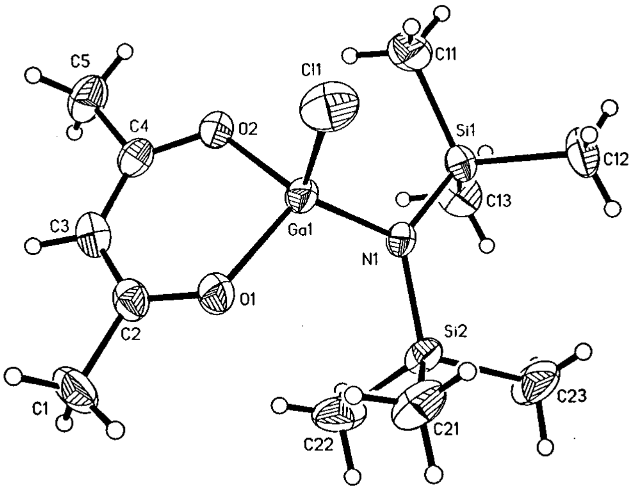

Figure 2. Molecular geometry and labeling of atoms for GaCl[N(SiMe$_3$)$_2$](acac) (30% probability ellipsoids for non-hydrogen atoms, hydrogen atoms artifically reduced).

Table 2. Selected Bond Distances (Å) and Angles (deg) for GaCl[N(SiMe$_3$)$_2$](acac)

(A) Gallium−Ligand Distances			
Ga(1)−Cl(1)	2.158(2)	Ga(1)−O(1)	1.888(4)
Ga(1)−N(1)	1.838(4)	Ga(1)−O(2)	1.881(4)
(B) N−Si and Si−C Distances			
N(1)−Si(1)	1.727(4)	N(1)−Si(2)	1.732(4)
Si(1)−C(11)	1.856(7)	Si(2)−C(21)	1.851(6)
Si(1)−C(12)	1.873(7)	Si(2)−C(22)	1.862(7)
Si(1)−C(13)	1.865(7)	Si(2)−C(23)	1.851(7)
(C) Distances within the acac Chelate Ring			
O(1)−C(2)	1.275(8)	O(2)−C(4)	1.284(7)
C(2)−C(3)	1.382(10)	C(3)−C(4)	1.378(9)
(D) Angles around Gallium			
Cl(1)−Ga(1)−O(1)	105.5(1)	O(1)−Ga(1)−O(2)	96.1(2)
Cl(1)−Ga(1)−O(2)	106.5(1)	O(1)−Ga(1)−N(1)	112.4(2)
Cl(1)−Ga(1)−N(1)	118.2(1)	O(2)−Ga(1)−N(1)	115.5(2)
(E) Angles around N(1)			
Ga(1)−N(1)-Si(1)	117.5(2)	Si(1)−N(1)-Si(2)	126.0(2)
Ga(1)−N(1)-Si(2)	116.4(2)		

room temperature and had sharp melting points, whereas GaEtCl(acac) and GaMe[N(SiMe$_3$)$_2$](acac) were liquids with well-defined, reproducible boiling points. The fifth compound, GaCl[N(SiMe$_3$)$_2$](acac), was a crystalline solid at room temperature, but it decomposed before it melted. The ^{1}H and ^{13}C NMR spectra of benzene solutions of the compounds were representative of pure, single compounds, as the spectrum of each compound had only one resonance for each type of substituent or ligand. The IR spectrum of each compound was indicative of chelation of the acetylacetonato ligand,[6] as the C−O stretching vibration for each was in the range of 1560−1595 cm^{-1}.

Two of the five gallium compounds with three different ligands, GaMeCl(acac) and GaCl[N(SiMe$_3$)$_2$](acac), were characterized by X-ray structural studies. The compound GaMeCl(acac) exists in the solid state as a monomeric, single species with a four-coordinate gallium atom. The molecular structure is shown in Figure 1, while selected interatomic distances and angles are collected in Table 1. The central gallium(III) atom has a distorted-tetrahedral environment. The acac ligand is bonded symmetrically (Ga(1)−O(2) = 1.901(7) Å and Ga(1)−O(4) = 1.878(7) Å), and this chelate ligand is associated with the smallest interatomic angle about gallium of O(2)−Ga(1)−O(4) = 96.3(3)°. These Ga−O bond distances are shorter than those found for the hexacoordinate derivative Ga(acac)$_3$, which range from 1.941(7) to 1.964(6) Å (average 1.952(7) Å).[7] The Ga−Cl bond distance of 2.181(4) Å is comparable to those observed for other asymmetrically substituted, monomeric compounds such as GaClMe[HB(3,5-Me$_2$pz)$_3$],[8] with a distance of 2.259(3) Å, and GaClMes*([N(SiMe$_3$)$_2$][9] (Mes* = 2,4,6-tri-*tert*-butylphenyl), at 2.228(4) Å. The Ga−C bond distance of 1.925(12) Å is typical of other methylgallium derivatives, including {GaClMe[N(H)(SiMe$_3$)]}$_2$[10] (1.956(11) Å) and GaClMe[HB(3,5-Me$_2$pz)$_3$][8] (1.93(1) Å).

The compound GaCl[N(SiMe$_3$)$_2$](acac) was also a monomeric, single species with tetracoordinate gallium in the solid state. The molecular geometry is shown in Figure 2. Interatomic distances and angles are collected in Table 2. The central gallium(III) atom has a distorted-tetrahedral coordination geometry with Ga−Cl = 2.158(2) Å, Ga−N(SiMe$_3$)$_2$ = 1.838(4) Å, and Ga−O(acac) =

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1.881(4) and 1.888(4) Å. The acac ligand is symmetrical, with a O(1)−Ga(1)−O(2) angle of 96.1(2)°. The nitrogen center of the $N(SiMe_3)_2$ ligand is planar, with N−Si bond distances of 1.727(4) and 1.732(4) Å and an Si(1)−N(1)−Si(2) angle of 126.0(2)°. The Ga−O bond distance (1.881(4) Å) is not significantly shorter than that of 1.901(7) Å found for GaMeCl(acac). The Ga−Cl distance of 2.158(2) Å is consistent with the Ga−Cl bond lengths in other monomeric compounds. The Ga−N bond distance of 1.838(4) Å for $GaCl[N(SiMe_3)_2](acac)$ is noteworthy, as it is slightly shorter than those observed for other gallium compounds that contain the hexamethyldisilazinato ligand, including the monomeric three-coordinate species $Ga[N(SiMe_3)_2]_3$ (average 1.863(5) Å[11] and average 1.868(1) Å[12]), $GaCl[N(SiMe_3)_2]_2$ (1.844(4), 1.834(4) Å[12]), and $GaClMes^*[N(SiMe_3)_2]$ (Mes* = 2,4,6-tri-*tert*-butylphenyl; 1.867(10) Å[9]). The coordination geometry about gallium suggests that the short Ga−N distance in this four-coordinate gallium amide may be due to electrostatic attractions rather than p−p π bonding.[14]

Gallium compounds with hexafluoropentanedionato ligands, GaRCl(hfac) (R = Me, Et, Mes), were unstable at room temperature and decomposed to unidentified, highly colored products. The relative rates of decomposition were GaMesCl(hfac) (slowest) < GaMeCl(hfac) ≪ GaEtCl(hfac). The derivative GaMesCl(hfac) required weeks to decompose while being stored at room temperature either under vacuum or in a sealed vial under an argon atmosphere in the drybox, whereas GaMeCl(hfac) decomposed over a period of days. The ethyl derivative was sufficiently unstable that it could not be isolated and characterized. Even though GaMeCl(hfac) and GaMesCl(hfac) were unstable at room temperature, they had sufficient stability that excellent analytical data for percent carbon and hydrogen were obtained from a commercial laboratory. The synthesis of GaEtCl(hfac) was attempted by a stoichiometric metathetical reaction between $GaEtCl_2$ and Na(hfac) in diethyl ether and in pentane and by an ethane elimination reaction between $GaEt_2Cl$ and H(hfac) in the absence of solvent. The only identified product from these reactions was $Ga(hfac)_3$,[1] a product consistent with the occurrence of a ligand redistribution reaction.

The synthesis of GaMeEt(acac) was attempted in order to determine whether the 2,4-pentanedionato ligand could stabilize a derivative with two different organic substituents. After experimental results demonstrated that LiMe reacted exclusively at the gallium atom in GaMeCl(acac) and not at the carbonyl group of the β-diketonato ligand, GaEtCl(acac) was reacted with LiMe. The observed products were an inseparable mixture of GaMeEt(acac) (∼60%), $GaMe_2(acac)$ (∼30%), and $GaEt_2(acac)$ (∼10%). Additional experiments demonstrated that GaMeEt(acac) did not decompose to $GaMe_2(acac)$ and $GaEt_2(acac)$ and $GaMe_2(acac)$[1] did not react with $GaEt_2(acac)$[1] to form GaMeEt(acac) after 6 months at room temperature and 1 week at 70 °C. Thus, $GaMe_2(acac)$ and $GaEt_2(acac)$ were not formed from GaMeEt(acac) by a ligand redistribution reaction but were products of a reaction between GaEtCl(acac) and LiMe.

Experimental Section

All compounds described in this investigation were sensitive to oxygen and moisture and were manipulated either under a purified argon atmosphere in a Vacuum Atmospheres drybox or by using standard vacuum line techniques. The starting materials $GaMeCl_2$,[13] $GaEtCl_2$,[14] $GaMesCl_2$,[15] and $GaMes_2Cl$[15] were prepared by literature methods. The β-diketones were purchased from Aldrich Chemical Co., dried over K_2CO_3, and vacuum-distilled prior to use. The metal β-diketonate reagents Li(acac), Na(acac), and Na(hfac) were prepared by reacting an excess of the diketone with either Li(n-Bu) or NaH in pentane at room temperature.[1] All solvents were carefully dried by using conventional procedures. Elemental analyses were performed by E&R Microanalytical Laboratory, Parsippany, NJ. Melting points were determined with a Mel-Temp by using flame-sealed capillaries filled with argon and are uncorrected. Infrared spectra of solids as Nujol mulls and of neat liquids between CsI plates were recorded by using a Perkin-Elmer 683 spectrometer. ^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were recorded with a Varian Unity-Nova 500 spectrometer. Proton chemical shifts are reported in δ (ppm) units and are referenced to $SiMe_4$ at δ 0.00 ppm and C_6D_5H at δ 7.15 ppm. Carbon chemical shifts are referenced to $SiMe_4$ at δ 0.00 ppm and to C_6D_6 at δ 128.39 ppm. All samples for NMR spectra were contained in flame-sealed NMR tubes. Molecular weights were measured cryoscopically by using an instrument similar to that described by Shriver and Drezdon.[16]

Preparation of GaMeCl(acac) by Metathesis. A flask equipped with a magnetic stirbar and a side-arm dumper that contained 2.13 g of Na(acac) (17.4 mmol) was charged with 2.70 g of $GaMeCl_2$ (17.3 mmol) and was connected to a Schlenk flask by a medium-porosity sintered-glass frit. Approximately 30 mL of benzene was then added to $GaMeCl_2$ by vacuum distillation. The flask was warmed to room temperature, and Na(acac) was added to the colorless $GaMeCl_2$/benzene solution over a period of 10 min. After the reaction mixture had been stirred for 12 h, the colorless solution was separated from the insoluble solid (NaCl) by filtration. The benzene was removed by vacuum distillation at room temperature to leave GaMeCl(acac) as a colorless benzene-soluble solid. The solid was sublimed under vacuum at 50 °C/10^{-3} mmHg through a glass elbow into a Schlenk flask, and 3.36 g of pure GaMeCl(acac) (15.3 mmol, 88.4% based on $GaMeCl_2$) was isolated.

GaMeCl(acac): colorless crystalline solid; mp 58.0−60.2 °C; soluble in pentane, benzene, and Et_2O; cryoscopic molecular weight, benzene solution. Formula weight 219.32 (observed molality, observed mol wt, association): 0.0737, 224.08, 1.02; 0.0631, 209.26, 0.95; 0.0482, 203.33, 0.93. Anal. Calcd for $C_6H_{10}ClGaO_2$: C, 32.86; H, 4.60; Cl, 16.16. Found: C, 33.02; H, 4.84; Cl, 16.27. ^1H NMR (C_6D_6, δ): 4.86 (0.5 H, acac H), 1.44 (6 H, acac CH_3), 0.17 (3 H, $GaCH_3$). ^{13}C NMR (C_6D_6, δ): 195.10 (C=O), 102.58 (=CH), 27.15 (acac CH_3), Ga−CH_3 not observed. IR (Nujol mull, C=O/C=C region, cm^{-1}): 1560 (br, vs), 1535 (vs), 1420 (br, vs), 1365 (vs), 1288 (vs), 1220 (m). Crystallographic quality crystals were grown by slow vacuum sublimation at 30 °C/10^{-3} mmHg.

Collection of X-ray Diffraction Data and Structural Solution for GaMeCl(acac). A crystal of approximate orthogonal dimensions 0.3 × 0.3 × 0.5 mm was sealed into a thin-walled glass capillary under an argon atmosphere inside the drybox, mounted, and then centered on a Siemens R3m/V

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automated four-circle diffractometer. The unit cell parameters were determined as described previously.[17] The Laue symmetry (C_i or $\bar{1}$) indicated that the crystal belonged to the triclinic system. Possible space groups are the noncentrosymmetric $P1$ (No. 1)[18a] or the centrosymmetric $P\bar{1}$ (No. 2).[18b] The latter was selected on the basis of intensity statistics ($\langle E^2 - 1\rangle = 0.771$ etc.), [19] frequency of occurrence data,[20] and probability of production from achiral precursors.[21] The selection of this higher space group was later confirmed as correct by the successful solution of the structure. It should be noted that the crystal used for the diffraction study (and all others previously examined) showed an unusually large mosaic spread; this rendered automatic centering operations very difficult and suggested that an elegant structural analysis would not be forthcoming. A full sphere of data (*i.e.*, two equivalent forms) with $2\theta = 6.0-45.0°$ was collected and corrected for absorption. The resulting 2398 reflections were merged to a unique data set of 1212 reflections with unexpectedly pleasing averaging statistics ($R_{\text{int}} = 0.98\%$). Details appear in Table 3.

All crystallographic calculations were carried out on a VAX station computer with the use of the Siemens SHELXTL PLUS (Release 4.11 (VMS)) program package.[22] The analytical scattering factors for neutral atoms[23a] were corrected for the $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[23b] The structure was solved via a combination of Patterson synthesis, difference Fourier syntheses, and least-squares refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from a difference Fourier map; their positions were optimized with $d(\text{C}-\text{H}) = 0.96$ Å[24] and their U's were refined in blocks according to the methyl group to which they belonged. Refinement converged with $R = 8.34\%$ for those data with $|F_o| > 6\sigma(|F_o|)$.

Preparation of GaEtCl(acac) by Metathesis. This compound was prepared in a manner analogous to that described for GaMeCl(acac) with the following modifications. The reagents 0.874 g of GaEtCl_2 (5.15 mmol) and 0.641 g of Na(acac) (5.25 mmol) were combined in benzene at room temperature. The product mixture was filtered, and benzene was removed by room-temperature vacuum distillation to leave GaEtCl(acac) as a colorless, benzene-soluble liquid. Pure GaEtCl(acac) (0.968 g, 4.15 mmol, 80.5% based on GaEtCl_2) was collected after a short-path distillation under dynamic vacuum with a water bath temperature of 40 °C and a head temperature of 28−30 °C.

GaEtCl(acac): colorless liquid; soluble in pentane, benzene, and Et_2O; cryoscopic molecular weight, benzene solution. Formula weight 233.34 (observed molality, observed mol wt, association): 0.0813, 228.88, 0.98; 0.0628, 221.53, 0.95; 0.0468, 215.63, 0.92. Anal. Calcd for $\text{C}_7\text{H}_{12}\text{ClGaO}_2$: C, 36.03; H, 5.18; Cl, 15.19. Found: C, 35.83; H, 5.19; Cl, 15.02. ^{1}H NMR (C_6D_6, δ): 5.01 (0.5 H, acac H), 1.54 (6 H, acac CH_3), 1.17 (t, $J_{\text{CH}} = 8$ Hz, 2.4 H, $\text{GaCH}_2\text{C}H_3$), 0.82 (q, $J_{\text{CH}} = 8$ Hz, 2 H, $\text{GaC}H_2\text{CH}_3$). ^{13}C NMR (C_6D_6, δ): 195.31 (C=O), 102.71 (=CH), 27.30 (acac CH_3), 9.10 ($\text{GaCH}_2\text{C}H_3$), 4.75 (br, $\text{Ga}C\text{H}_2\text{CH}_3$). IR (neat, C=O/C=C region, cm^{-1}): 1565 (br, vs), 1525 (br, vs), 1435 (s), 1355 (vs), 1287 (s), 1207 (w), 1190 (w).

Table 3. Data for X-ray Crystallographic Studies of GaMeCl(acac) and GaCl[N(SiMe$_3$)$_2$](acac)

	GaMeCl(acac)	GaCl[N(SiMe$_3$)$_2$]-(acac)
mol formula	$\text{C}_6\text{H}_{10}\text{ClGaO}_2$	$\text{C}_{11}\text{H}_{25}\text{ClGaNO}_2\text{Si}_2$
M_r	219.3	364.7
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)
a, Å	7.535(7)	15.892(5)
b, Å	7.604(4)	13.611(4)
c, Å	8.744(6)	17.568(5)
α, deg	112.02(5)	90.000
β, deg	91.70(7)	90.000
γ, deg	93.95(6)	90.000
V, Å^3	462.5(6)	3800(2)
D_{calcd}, g/cm^3	1.575	1.275
Z	2	8
μ(Mo Kα), mm^{-1}	3.201	1.704
T (K)	296	296
F(000)	220	1520
2θ range, deg	6.0−45.0	5.0−45.0
h	−8 to +8	−17 to 0
k	−8 to +8	−14 to 0
l	−9 to +9	−18 to +18
no. of rflns collected	2398	5396
no. of indep rflns	1212 (R_{int} = 0.98%)	2490 (R_{int} = 2.34%)
no. of rflns used for refinement	972 (>6σ)	1568 (>4σ)
weighting scheme, w^{-1}	$\sigma^2(F) + 0.0595F^2$	$\sigma^2(F) + 0.0012F^2$
χ(secondary extinction)	not required	0.00064(7)
$T_{\text{max}}/T_{\text{min}}$	0.3360/0.2222	n/a
no. of refined params	95	167
final R indices (all data),[a] %		
R	9.29	6.93
R_w	14.18	5.64
final R indices (obsd data),[a] %		
R	8.34	3.47
R_w	10.25	4.39
goodness of fit	0.43	0.88
largest, mean Δ/σ	0.001, 0.000	0.015, 0.003
data to param ratio	10.2:1	9.4:1
largest diff peak, e Å^{-3}	+1.91	+0.30
largest diff hole, e Å^{-3}	−1.72	−0.23

[a] R indices are defined as follows: $R\ (\%) = 100\sum||F_o| - |F_c||/\sum|F_o|$; $R_w\ (\%) = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Preparation of GaMesCl(acac) by Metathesis. This compound was prepared in a manner analogous to that described for GaMeCl(acac) with the following modifications. The reagents 0.664 g of GaMesCl_2 (2.55 mmol) and 0.313 g of Na(acac) (2.56 mmol) were combined in Et_2O at room temperature. The product mixture was filtered, and the ether was removed from the solution by room-temperature vacuum distillation to leave GaMesCl(acac) as a colorless crystalline solid. Recrystallization of a pentane solution at −30 °C produced 0.759 g of GaMesCl(acac) (2.35 mmol, 91.8% based on GaMesCl_2).

GaMesCl(acac): colorless crystalline solid; soluble in benzene and toluene but only slightly soluble in pentane; mp 109.7−110.8 °C. Cryoscopic molecular weight, benzene solution, formula weight 323.47 (observed molality, observed mol wt, association): 0.0774, 330.60, 1.02; 0.0552, 327.83, 1.01; 0.0388, 322.93, 1.00. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{ClGaO}_2$: C, 51.98; H, 5.61. Found: C, 51.77; H, 5.65. ^{1}H NMR (C_6D_6, δ): 6.78 (1.3 H, Mes H), 4.91 (0.5 H, acac-H), 2.65 (6 H, o-Mes-CH_3), 2.13 (3 H, *p*-Mes CH_3), 1.48 (6 H, acac CH_3). ^{13}C NMR (C_6D_6, δ): 194.95 (C=O), 145.12 (Mes), 139.94 (Mes), 128.68 (Mes), Ga−C(Mes) not observed, 102.58 (=C− (acac)), 27.15 (acac CH_3), 25.22 (*o*-Mes CH_3), 21.61 (*p*-Mes CH_3). IR (Nujol mull, C=O/C=C region, cm^{-1}): 1595 (m), 1555 (vs), 1540 (vs), 1520 (vs), 1455 (vs), 1370 (s), 1358 (s), 1343 (s), 1237 (s).

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Preparation of GaMesCl(acac) by a Ligand Redistribution Reaction. A colorless benzene solution (15 mL) of 0.24 g of $GaMes_2(acac)$ (0.58 mmol) and 0.14 g of $GaCl_2(acac)$ (0.58 mmol) was stirred for 20 h at room temperature. The benzene was removed by vacuum distillation at room temperature, and 0.33 g of a colorless solid (mp 101.4−106.7 °C) was isolated. This solid was then recrystallized from pentane at −30 °C to yield 0.21 g of pure GaMesCl(acac) (0.65 mmol, 56% yield) (mp 108.2−110.5 °C). The small scale of this reaction with the corresponding mechanical loss of product probably accounts for the low yield when compared to the metathetical reaction.

Preparation of GaMe[N(SiMe$_3$)$_2$](acac) by Metathesis. A typical preparation utilized 0.604 g of GaMeCl(acac) (2.76 mmol), 0.461 g of $LiN(SiMe_3)_2$ (2.76 mmol), and Et_2O. The reagents were combined and stirred for 2 h at −78 °C, during which time the color of the reaction mixture changed from colorless to light yellow. The cloudy, pale yellow reaction mixture was then warmed to room temperature and was stirred for an additional 15 h. After the yellow Et_2O-soluble fraction had been separated from the yellowish insoluble solid by filtration, the volatile components were removed from the solution by vacuum distillation at room temperature. Purification of the product by using a short-path distillation apparatus under dynamic vacuum and a bath temperature of 50 °C and a head temperature of 45−47 °C provided 0.812 g of pure $GaMe[N(SiMe_3)_2](acac)$ (2.36 mmol, 85.7% yield based on GaMeCl(acac)).

GaMe[N(SiMe$_3$)$_2$](acac): light yellow liquid at room temperature; soluble in pentane, benzene, and diethyl ether. Cryoscopic molecular weight, benzene solution, formula weight 344.25 (observed molality, observed mol wt, association): 0.0886, 341, 0.99; 0.0660, 337, 0.98; 0.0405, 335, 0.97. Anal. Calcd for $C_{12}H_{28}GaNO_2Si_2$: C, 41.87; H, 8.20; N, 4.07. Found: C, 41.96; H, 8.18; N, 4.13. ^1H NMR (C_6D_6, δ): 4.91 (0.5 H, acac H), 1.54 (6 H, acac CH_3), 0.35 (18 H, Si−CH_3), 0.13 (3 H, Ga−CH_3). ^{13}C NMR (C_6D_6, δ): 193.61 (C═O), 101.44 (═CH), 27.44 (acac-CH_3), 5.48 (Si−CH_3), −4.65 (br, Ga−CH_3). IR (neat, C═O/C═C region, cm^{-1}): 1587 (vs), 1525 (vs), 1430 (s), 1370 (vs), 1282 (s), 1258 (vs), 1245 (vs), 1207 (m), 1192 (w).

Preparation of GaCl[N(SiMe$_3$)$_2$](acac) by Metathesis. In one experiment, 0.468 g of $Li[N(SiMe_3)_2]\cdot Et_2O$ (1.94 mmol) was added at room temperature over a period of 20 min to a colorless benzene solution of 0.465 g of $GaCl_2(acac)$ (1.94 mmol). The reaction mixture became yellow within a few minutes of mixing the reagents. After the reaction mixture had been stirred at room temperature for 12 h, the solvent was removed by vacuum distillation to leave a viscous yellow liquid. Then, 10−15 mL of pentane was added to the yellow liquid and, upon warming, a light yellow solution above a solid was observed. The mixture was filtered. The resulting solution was cooled to −30 °C for 12 h, and a yellow powder formed. A total of three extractions and crystallizations produced 0.363 g of pure $GaCl[N(SiMe_3)_2](acac)$ (0.995 mmol, 51.4% based on $GaCl_2(acac)$).

GaCl[N(SiMe$_3$)$_2$](acac): yellow solid; soluble in benzene and slightly soluble in pentane; mp 72.3−74.6 °C dec. Cryoscopic molecular weight, benzene solution, formula weight 364.67 (observed molality, observed mol wt, association): 0.0756, 370, 1.01; 0.0545, 368, 1.00; 0.0393, 367, 1.00. Anal. Calcd for $C_{11}H_{25}ClGaNO_2Si_2$: C, 36.23; H, 6.91; N, 3.84; Found: C, 36.19; H, 6.88; N, 3.71. ^1H NMR (C_6D_6, δ): 4.79 (0.5 H, acac H), 1.39 (6 H, acac CH_3), 0.41 (18 H, $SiCH_3$). ^{13}C NMR (C_6D_6, δ): 195.63 (C═O), 102.64 (═CH), 27.21 (acac CH_3), 5.15 ($SiCH_3$). IR (Nujol mull, C═O/C═C region, cm^{-1}): 1565 (vs), 1545 (sh, vs), 1528 (vs), 1450 (s), 1395 (sh, m), 1355 (vs), 1303 (sh, m), 1289 (s), 1260 (sh, s), 1247 (vs). Crystallographic quality crystals were grown by vacuum sublimation at 55 °C.

Collection of X-ray Diffraction Data and Structural Solution for GaCl[N(SiMe$_3$)$_2$](acac). A well-defined crystal of approximate orthogonal dimensions 0.2 × 0.2 × 0.4 mm was sealed into a thin-walled glass capillary as described above. The crystal was mounted with its extended direction close to collinear with the Φ axis of a Siemens R3m/V automated four-circle diffractometer. The Laue symmetry (D_{2h} or mmm) indicated the orthorhombic crystal system. The systematic absences ($0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, $hk0$ for $h = 2n + 1$) uniquely define the common centrosymmetric orthorhombic space group $Pbca$ (No. 61).[18c] Two equivalent forms of data (hkl and h$k\bar{l}$) were collected. The 5396 data were merged to a unique set of 2490 data (with $R_{int} = 2.34\%$), of which 1568 data with $|F_o| > 4.0\sigma(|F_o|)$ were considered "observed". Details are provided in Table 3.

Preparation of GaMeCl(hfac) by Metathesis. A Solv-Seal flask equipped with a magnetic stirbar and a side-arm dumper that contained 0.726 g of Na(hfac) (3.15 mmol) was charged with 0.509 g of $GaMeCl_2$ (3.27 mmol). The flask was connected to a second Schlenk flask by a medium-porosity glass frit. After 20 mL of pentane was added to the $GaMeCl_2$ by vacuum distillation, Na(hfac) was added to the colorless pentane solution at room temperature over a period of 10 min. The reaction mixture was stirred for 12 h, and then the pentane-soluble and -insoluble components were separated by filtration. The pentane-insoluble solid (NaCl) was washed once with pentane, and then the components volatile at 0 °C were removed by vacuum distillation from the soluble fraction. The pentane-soluble product was purified by vacuum distillation at room temperature, and 0.679 g of GaMeCl(hfac) (2.07 mmol, 65.8% based on $GaMeCl_2$) as a colorless liquid was collected in a preweighed tube. The compound slowly turned orange when stored under vacuum at room temperature for 2 days. The following characterization data were obtained for the original colorless liquid.

GaMeCl(hfac): colorless liquid with a freezing point below −20 °C; soluble in pentane and benzene. Vapor pressure at 20 °C: 2.3 mmHg. Cryoscopic molecular weight, benzene solution, formula weight 327.26 (observed molality, observed mol wt, association): 0.0610, 336.0, 1.03; 0.0483, 334.0, 1.02; 0.0361, 332.2, 1.02. Anal. Calcd for $C_6H_4ClF_6GaO_2$: C, 22.02; H, 1.23. Found: C, 22.16; H, 1.25. ^1H NMR (C_6D_6, δ): 5.86 (s, 0.7 H, hfac H), − 0.15 (Ga−CH_3, 3 H). ^{13}C NMR (C_6D_6, δ): 182.40 (q, $J_{CO-F} = 37.8$ Hz, −C═O), 117.39 (q, $J_{C-F} = 285$ Hz, −CF_3), 93.78 (s, ═C−), −7.60 (s, br, Ga−CH_3). IR (neat, cm^{-1}): 1738 (w), 1700 (w), 1648 (vs), 1623 (vs), 1570 (vs), 1547 (s), 1512 (m), 1509 (m), 1491 (w), 1468 (m), 1441 (sh, vs), 1438 (sh, vs), 1430 (vs), 1360 (m), 1344 (sh, w), 1255 (br, vs). IR (gas cell, 2.0 mmHg, cm^{-1}): 1650 (vs), 1638 (vs), 1591 (w), 1573 (m), 1550 (m), 1515 (w), 1434 (vs), 1363 (w), 1260 (vs).

Preparation of GaMeCl(hfac) by a Methane Elimination Reaction. A flask equipped with a magnetic stir bar and charged with 1.20 g of $GaMe_2Cl$ (8.89 mmol) was connected to a Schlenk flask by a glass elbow. After pentane (∼25 mL) and 1.85 g of H(hfac) (8.89 mmol) were added by vacuum distillation, the reaction mixture was stirred for 12 h at room temperature. The components of the product mixture that were volatile at 0 °C were removed by vacuum distillation. Pure GaMeCl(hfac) as a colorless liquid (2.73 g, 8.34 mmol, 94.0% yield) was collected by vacuum distillation at room temperature into a preweighed tube. The characterization data of this colorless liquid were identical with that prepared by the metathetical reaction.

Preparation of GaMesCl(hfac) by Metathesis. This compound was prepared in a manner similar to that described for GaMeCl(hfac), with the following modifications. The reagents $GaMesCl_2$ (0.550 g, 2.12 mmol) and Na(hfac) (0.491 g, 2.13 mmol) were combined in 30 mL of Et_2O at room temperature and stirred for 15 h. The Et_2O was removed, and 30 mL of pentane was added by vacuum distillation. Then, the pentane-soluble components were separated from the insoluble NaCl and excess Na(hfac) by filtration. Removal of pentane by vacuum distillation left 0.803 g of GaMesCl(hfac) (1.86 mmol, 87.9% based on $GaMesCl_2$) as a pentane-soluble, light yellow crystalline solid. The compound slowly turned brownish violet when stored for 1 month at room temperature either in a closed vial under an argon atmosphere in the drybox or under vacuum.

GaMesCl(hfac): light yellow solid; soluble in pentane and benzene; mp 62.8−64.6 °C. Cryoscopic molecular weight, benzene solution, formula weight 431.41 (observed molality, observed mol wt, association): 0.0570, 475, 1.10; 0.0440, 461, 1.07; 0.0346, 455, 1.06. Anal. Calcd for $C_{14}H_{12}ClF_6GaO_2$: C, 38.98; H, 2.80. Found: C, 38.83; H, 2.88. ^1H NMR (300 MHz, C_6D_6, δ): 6.28 (s, 2 H, Mes H), 5.81 (s, 0.7 H, hfac H), 2.35 (6 H, o-Mes CH_3), 2.04 (3 H, *p*-Mes CH_3). ^{13}C NMR (C_6D_6, δ): 181.79 (q, $J_{CO-F} = 37.2$ Hz, $-C{=}O$), 144.73 (Mes C═), 141.46 (Mes C═), 128.68 (Mes C═), 117.28 (q, $J_{C-F} = 284$ Hz, $-CF_3$), 93.82 (s, hfac ═C), 24.79 (*o*-Mes CH_3), 21.43 (*p*-Mes CH_3). IR (neat, cm^{-1}): 1639 (m), 1616 (m), 1596 (m), 1580 (sh, w), 1565 (m), 1537 (m), 1505 (w), 1455 (m), 1422 (m), 1360 (m), 1288 (w).

Reaction of GaMeCl(acac) with LiMe in a 1:1 Mole Ratio. Preparation of GaMe$_2$(acac). A Solv-Seal flask equipped with a magnetic stir bar was charged with 0.789 g of GaMeCl(acac) (3.60 mmol) and was connected to a Solv-Seal flask by a medium-porosity glass frit. Then a tube that contained 3.6 mmol of an ether solution of LiMe (2.6 mL, 1.4 M in Et_2O) was connected to the reaction flask. Next, approximately 20 mL of Et_2O was vacuum-distilled onto the GaMeCl(acac). The LiMe solution was added to the stirred colorless Ga(Me)(Cl)(acac) solution at room temperature, and a colorless solid formed immediately. After the reaction mixture had been stirred for 4 h, the soluble and insoluble components were separated by filtration. The Et_2O-soluble fraction was cooled to −20 °C, and the Et_2O was removed by vacuum distillation and passed through a −20 °C trap and into a −196 °C trap. Some colorless crystalline solid remained in the flask held at −20 °C, whereas more collected in the −20 °C trap. These fractions were combined and identifed by its melting point[1] and ^1H NMR spectrum[1] as $GaMe_2$(acac) (0.399 g, 2.01 mmol, 56% yield based on GaMeCl(acac)).

Reaction of GaMeCl(acac) and LiMe in a 1:2 Mol Ratio. Preparation of $GaMe_3 \cdot OEt_2$. Reaction of 6.3 mmol of LiMe (4.5 mL of 1.4 M in Et_2O) with 0.652 g of GaMeCl(acac) (2.97 mmol) in 25 mL of Et_2O produced soluble and insoluble products that were separated by filtration. The Et_2O-soluble portion of the reaction mixture was cooled to −20 °C, and the Et_2O was removed by vacuum distillation. The colorless liquid remaining in the −20 °C flask was identified as $GaMe_3 \cdot Et_2O$[25] by comparing its ^1H NMR spectrum (^1H NMR (400 MHz, C_6D_6, δ): 3.20 (q, $J = 7$ Hz, 6 H, OCH_2CH_3), 0.84 (t, $J = 7$ Hz, OCH_2CH_3), −0.06 (s, 9 H $GaCH_3$)) with the spectrum of a known sample of $GaMe_3 \cdot Et_2O$. This colorless liquid smoked upon exposure to air.

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Supporting Information Available: Complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and calculated positions for hydrogen atoms and packing diagrams for the two compounds studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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