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Chemistry of Some Dihalogallium(III) β-Diketonate Derivatives. Crystal and Molecular Structures of $GaCl_2$(acac), $GaCl_2$(tmhd), and [*trans*-$Ga(acac)_2(THF)_2^+$][$GaCl_4^-$]

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The dichlorogallium(III) β-diketonato derivatives $GaCl_2$(bdk) [bdk = acac (2,4-pentanedionato) and tmhd (2,2,6,6-tetramethylheptanedionato)] have been prepared and characterized in hydrocarbon solutions by NMR spectral studies and cryoscopic molecular weight measurements and in the solid state by X-ray structural studies. These compounds, which have chelated β-diketonato ligands and four-coordinate gallium, react with THF to form species of composition $GaCl_2$(bdk)·THF. A single-crystal X-ray diffraction study identified $GaCl_2$(acac)·THF as the ion-pair [*trans*-$Ga(acac)_2(THF)_2^+$][$GaCl_4^-$]. The gallium atom in the cation is six-coordinate, whereas in the anion it is four-coordinate. Variable-temperature ^1H NMR spectral studies in CD_2Cl_2 solution suggest that multiple processes including (i) a stereochemical rearrangement, (ii) THF exchange, and (iii) equilibria between [$Ga(bdk)_2(THF)_2^+$][$GaCl_4^-$], $GaCl_2$(bdk), and at least one other species such as [$Ga(bdk)_2(THF)^+$][$GaCl_4^-$] are occurring in solution. In contrast, GaX_2(hfac) (X = Cl, Br; hfac = 1,1,1,5,5,5-heaxafluoro-2,4-pentanedionato) cannot be isolated because these compounds undergo ligand redistribution reactions to form $Ga(hfac)_3$ (~80% yields).

Introduction

The uninegative, bidentate β-diketonato ligands, 2,4-pentanedionato (acac) and 2,2,6,6-tetramethylheptanedionato (tmhd), stabilize gallium(III)[1,2] and gallium(II)[3] compounds with three different substituents. In contrast, compounds with the 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato ligand (hfac) decompose by undergoing ligand redistribution reactions to form $Ga(hfac)_3$.[2] As dichlorogallium(III) β-diketonates, $GaCl_2$(bdk), should be useful starting materials for the preparation of other unsymmetrically substituted compounds, our goal was to investigate their chemistry. However, to our surprise, the nature of gallium compounds with this simplest formula had not been defined when this research was initiated, but there were numerous reports about an oily or waxy material with the simplest formula $AlCl_2$(acac).[4−7] An X-ray structural study[5] of an aluminum compound that crystallized from the oil identified the material as [$Al_2(acac)_3Cl_2^+$][$AlCl_4^-$] rather than the expected simple monomer with a single chelating acac ligand. The cation had two pentacoordinate aluminum centers. One aluminum atom in the cation had one terminal chloride ligand and two acac ligands, of which one oxygen from each formed a bridge to the other aluminum atom. The second aluminum atom in the cation had one chelated acac ligand, one terminal chloride ligand, and two bridging oxygen atoms. The anion had tetracoordinate aluminum. An extensive NMR spectral study[5] of CH_2Cl_2 solutions of the material with the simplest formula $AlCl_2$(acac) identified the existence of an equilibrium between [$Al_2(acac)_3Cl_2^+$][$AlCl_4^-$] and the simple monomeric species $AlCl_2$(acac). Solutions of $AlCl_2$(acac) reacted with THF to form [$Al(acac)_2(THF)_2^+$][$AlCl_4^-$].[6] The solid state structure of [$Al(acac)_2(THF)_2^+$][$AlCl_4^-$] revealed the trans isomer of the hexacoordinate aluminum cation,[7] whereas a CD_2Cl_2 solution existed as an equilibrium mixture of cis and trans isomers with the trans isomer being the predominant form (75%) at −50 °C.[6] In the following paper, the synthesis and characterization of gallium compounds with the simplest formula $GaCl_2$(bdk) (bdk = acac and tmhd) and some aspects of their chemistry are described.

Results and Discussion

The compounds with the simplest formula $GaCl_2$(bdk) (bdk = acac,[8] tmhd) were prepared in high yield at room temperature by utilizing a metathetical reaction between $GaCl_3$ and Na(bdk) in a 1:1 mol ratio in benzene.

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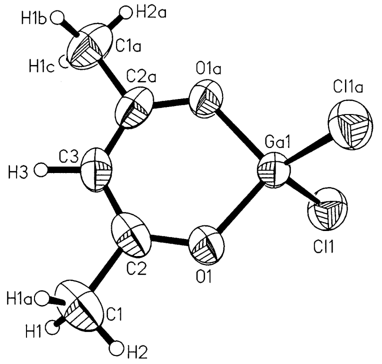

Figure 1. Molecular geometry and labeling of atoms for $GaCl_2(acac)$ (30% probability ellipsoids for non-hydrogen atoms, hydrogen atoms are artificially reduced). Note that the molecule possesses crystallographically imposed C_{2v} symmetry.

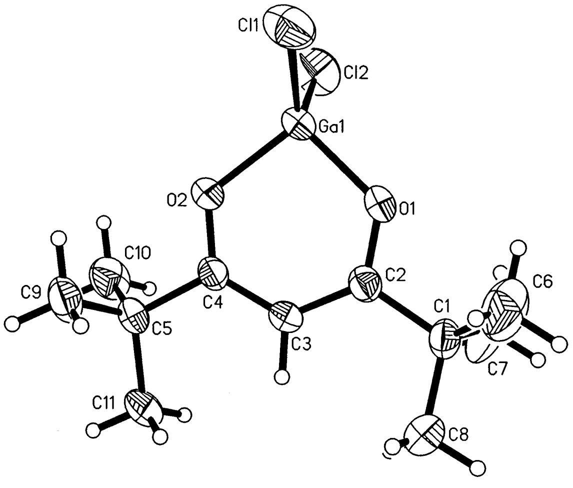

Figure 2. Molecular geometry and labeling of atoms for $GaCl_2(tmhd)$ (30% probability ellipsoids for non-hydrogen atoms, hydrogen atoms are artificially reduced).

Table 1. Selected Bond Distances (Å) and Angles (deg) for $GaCl_2(acac)$

Bond Distances			
Ga(1)−Cl(1)	2.115 (6)	Ga(1)−O(1)	1.835 (9)
Ga(1)−Cl(1A)	2.115 (6)	Ga(1)−O(1A)	1.835 (9)
O(1)−C(2)	1.289 (20)	C(1)−C(2)	1.498 (23)
C(2)−C(3)	1.366 (17)	C(3)−C(2A)	1.366 (17)

Bond Angles			
Cl(1)−Ga(1)−O(1)	110.0 (2)	Cl(1)−Ga(1)−Cl(1A)	116.1 (3)
O(1)−Ga(1)−Cl(1A)	110.0 (2)	Cl(1)−Ga(1)−O(1A)	110.0 (2)
O(1)−Ga(1)−O(1A)	99.3 (6)	Cl(1A)−Ga(1)−O(1A)	110.0 (2)
Ga(1)−O(1)−C(2)	122.3 (9)	O(1)−C(2)−C(1)	116.2 (13)
O(1)−C(2)−C(3)	124.7 (14)	C(1)−C(2)−C(3)	119.1 (15)
C(2)−C(3)−C(2A)	126.5 (20)		

Table 2. Selected Bond Distances (Å) and Angles (deg) for $GaCl_2(tmhd)$

Bond Distances			
Ga(1)−Cl(1)	2.124 (2)	Ga(1)−O(1)	1.849 (4)
Ga(1)−O(2)	1.841 (3)	O(1)−C(2)	1.286 (6)
O(2)−C(4)	1.284 (6)	Ga(1)−Cl(2)	2.129 (2)

Bond Angles			
Cl(1)−Ga(1)−Cl(2)	113.2 (1)	Cl(1)−Ga(1)−O(1)	111.1 (1)
Cl(2)−Ga(1)−O(1)	110.9 (1)	Cl(1)−Ga(1)−O(2)	112.4 (2)
Cl(2)−Ga(1)−O(2)	110.0 (1)	O(1)−Ga(1)−O(2)	98.2 (1)
Ga(1)−O(1)−C(2)	123.7 (2)	Ga(1)−O(2)−C(4)	123.5 (3)
O(1)−C(2)−C(1)	113.9 (3)	O(2)−C(4)−C(3)	123.6 (3)
O(1)−C(2)−C(3)	123.1 (4)	O(2)−C(4)−C(5)	113.8 (3)
C(3)−C(4)−C(5)	122.7 (4)		

Reactions in pentane produced significantly lower yields due to the lower solubilities of the products. Single-crystal X-ray structural studies of $GaCl_2(acac)$ and $GaCl_2(tmhd)$ revealed that each compound exists as a monomeric, four-coordinate species with one chelated β-diketonato ligand. These molecular geometries and labeling of the atoms are given in Figures 1 and 2, respectively. Interatomic distances and angles are collected in Tables 1 and 2, respectively. Both gallium(III) centers have distorted tetrahedral coordination geometries. The smallest angle about gallium in $GaCl_2(acac)$ is 99.3(6) Å for O(1)−Ga(1)−O(1a), whereas in $GaCl_2(tmhd)$ the smallest is 98.2(1)° for O(1)−Ga(1)−O(2). The acetylacetonate ligand in $GaCl_2(acac)$ has crystallographically imposed C_{2v} symmetry with Ga−O bond distances of 1.835(9) Å. The Ga−O bond distances in $GaCl_2(tmhd)$ are 1.849(4) and 1.841(3) Å and are statistically indistinguishable from each other. These distances are all shorter than those observed for $Ga(acac)_3$,[9] which average 1.952(7) Å, $GaMe_2(moppd)$[10] [moppd = *O,O′*-bis(4-methoxyphenyl)propane-1,3-dionato] at 1.921(2) Å (av), and $GaMes_2(hfac)$[1] (Mes = 2,4,6-mesityl) at 2.009 (11) Å (av). The Ga−Cl bond distances in $GaCl_2(acac)$ are both 2.115(6) Å, whereas the gallium−chlorine distances in $GaCl_2(tmhd)$ are 2.124(2) and 2.129(2) Å. These distances are comparable to those in other compounds with tetracoordinate gallium centers such as $(GaMeCl_2)_2$ (observed in the vapor phase)[11] at 2.129(3) Å and $[Ga(t\text{-}Bu)Cl_2]_2$[12] at 2.151(2) Å.

The characterization data for $GaCl_2(acac)$ and of $GaCl_2(tmhd)$ in solutions are consistent with the presence of monomeric species with four-coordinate gallium atoms for each. A cryoscopic molecular weight study of $GaCl_2(acac)$ in benzene solution suggested the presence of monomeric species only. The room-temperature ^1H and ^{13}C NMR spectra of both $GaCl_2(acac)$ and $GaCl_2(tmhd)$ in C_6D_6 had only one set of resonances for the β-diketonato ligand. Variable-temperature ^1H NMR spectroscopic studies of $GaCl_2(acac)$ at 0.2 and 0.7 m over the temperature range of 20 to −80 °C in both CD_2Cl_2 and toluene-d_8 solutions exhibited neither temperature nor concentration dependence. The IR spectra for $GaCl_2(acac)$ and $GaCl_2(tmhd)$ as Nujol mulls had broad C−O stretching bands centered at 1550 cm^{-1}. This C−O stretch was 25−40 cm^{-1} lower in energy than that observed for monomeric diorganogallium acetylacetonates (1575−1590 cm^{-1}).[1] Thus, all observations suggest that the β-diketonato ligands in $GaCl_2(acac)$ and $GaCl_2(tmhd)$ are chelated to a single gallium(III) atom, not bridging to form associated species or ion-pairs as in $AlCl_2(acac)$.[4−7]

Attempts were made to prepare $GaX_2(hfac)$ (X = Cl, Br) by metathetical, ligand redistribution and elimination reactions, but liquids identified as mixtures of products that contained $Ga(hfac)_3$[13] and possibly GaX_2-

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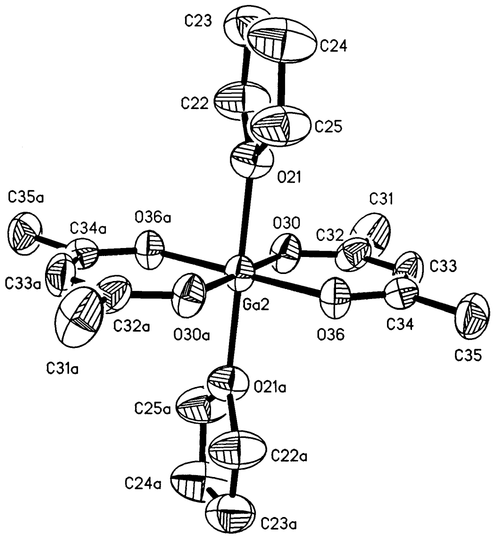

Figure 3. Molecular geometry and labeling of atoms for the more "ordered" [*trans*-Ga(acac)$_2$(THF)$_2$$^+$] cation in the [*trans*-Ga(acac)$_2$(THF)$_2$][GaCl$_4$] structure (30% probability ellipsoids for non-hydrogen atoms, hydrogen atoms are artificially reduced).

(hfac) were obtained in every case. Details of these experiments are provided with the Supporting Information. ^{1}H NMR spectra of benzene solutions of the mixtures, the physical properties of the mixtures, and the melting point of the colorless crystalline needles isolated from the mixtures demonstrated the presence of Ga(hfac)$_3$. The instability of GaX$_2$(hfac) (X = Cl, Br) at room temperature prevented its conclusive identification, but the presence of new ^{1}H NMR resonances at 5.44 (Cl) and 5.52 (Br) ppm that were observed for the crude products is consistent with these compounds. The instability of GaX$_2$(hfac) and the formation of Ga(hfac)$_3$ can be attributed to a ligand redistribution reaction that occurs because of the reduced Lewis basicity of the carbonyl group oxygen due to the electron-withdrawing effects of the fluorine atoms. The lower Lewis basicity permits a facile dissociation of a carbonyl group that provides an open coordination site on gallium for the occurrence of a ligand redistribution reaction.

The new compounds GaCl$_2$(bdk) (bdk = acac, tmhd) reacted with THF to produce colorless solids that had the simplest formula GaCl$_2$(bdk)·THF. These solids were soluble in CD$_2$Cl$_2$ and THF but only slightly soluble in benzene and pentane. Recrystallization of GaCl$_2$(acac)·THF from benzene provided a single crystal for an X-ray diffraction study that identified a six-coordinate gallium cation and a four-coordinate gallium anion, [*trans*-Ga(acac)$_2$(THF)$_2$$^+$][GaCl$_4$$^-$], rather than a five-coordinate adduct as in GaMe$_2$(hfac)·NC$_5$H$_5$.[1] There are two independent gallium cations, each with disordered THF ligands, in the unit cell. The coordination geometry and the labeling of the atoms for one of the gallium cations are given in Figure 3. Interatomic distances and angles are collected in Table 3. The crystallographic asymmetric unit consists of the following fragments:

(1) One-half of a [*trans*-Ga(acac)$_2$(THF)$_2$$^+$] cation (A) is centered on Ga(1) at the inversion center at 0, 0, 0. This cation suffers from disorder affecting the THF ligands.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [*trans*-Ga(acac)$_2$(THF)$_2$$^+$][GaCl$_4$$^-$]

Bond Distances			
Ga(1)−O(1)	2.031 (6)	Ga(1)−O(10)	1.908 (6)
Ga(1)−O(16)	1.904 (5)	Ga(1)−O(1A)	2.031 (6)
Ga(1)−O(10A)	1.908 (6)	Ga(1)−O(16A)	1.904 (5)
Ga(2)−O(21)	2.043 (5)	Ga(2)−O(30)	1.911 (5)
Ga(2)−O(36)	1.902 (5)	Ga(2)−O(21A)	2.043 (5)
Ga(2)−O(30A)	1.911 (5)	Ga(2)−O(36A)	1.902 (5)
Ga(3)−Cl(1)	2.154 (3)	Ga(3)−Cl(2)	2.159 (3)
Ga(3)−Cl(3)	2.150 (3)	Ga(3)−Cl(4)	2.130 (3)

Bond Angles			
O(1)−Ga(1)−O(10)	89.5 (2)	O(1)−Ga(1)−O(16)	90.7 (2)
O(10)−Ga(1)−O(16)	93.4 (2)	O(1)−Ga(1)−O(1A)	180.0 (−)
O(10)−Ga(1)−O(1A)	90.5 (2)	O(16)−Ga(1)−O(1A)	89.3 (2)
O(1)−Ga(1)−O(10A)	90.5 (2)	O(10)−Ga(1)−O(10A)	180.0 (−)
O(16)−Ga(1)−O(10A)	86.6 (2)	O(1A)−Ga(1)−O(10A)	89.5 (2)
O(1)−Ga(1)−O(16A)	89.3 (2)	O(10)−Ga(1)−O(16A)	86.6 (2)
O(16)−Ga(1)−O(16A)	180.0 (−)	O(1A)−Ga(1)−O(16A)	90.7 (2)
O(10A)−Ga(1)−O(16A)	93.4 (2)	O(21)−Ga(2)−O(30)	89.7 (2)
O(21)−Ga(2)−O(36)	90.3 (2)	O(30)−Ga(2)−O(36)	93.9 (2)
O(21)−Ga(2)−O(21A)	180.0 (−)	O(30)−Ga(2)−O(21A)	90.3 (2)
O(36)−Ga(2)−O(21A)	89.7 (2)	O(21)−Ga(2)−O(30A)	90.3 (2)
O(30)−Ga(2)−O(30A)	180.0 (−)	O(36)−Ga(2)−O(30A)	86.1 (2)
O(21A)−Ga(2)−O(30A)	89.7 (2)	O(21)−Ga(2)−O(36A)	89.7 (2)
O(30)−Ga(2)−O(36A)	86.1 (2)	O(36)−Ga(2)−O(36A)	180.0 (−)
O(21A)−Ga(2)−O(36A)	90.3 (2)	O(30A)−Ga(2)−O(36A)	93.9 (2)
Cl(1)−Ga(3)−Cl(2)	109.7 (1)	Cl(1)−Ga(3)−Cl(3)	108.5 (1)
Cl(2)−Ga(3)−Cl(3)	109.2 (1)	Cl(1)−Ga(3)−Cl(4)	109.6 (1)
Cl(2)−Ga(3)−Cl(4)	110.0 (1)	Cl(3)−Ga(3)−Cl(4)	109.7 (1)
Ga(1)−O(1)−C(2)	130.0 (9)	Ga(1)−O(1)−C(5)	133.0 (11)

(2) One-half of a [*trans*-Ga(acac)$_2$(THF)$_2$$^+$] cation (B) is centered on Ga(2) at the inversion center of coordinates (0, 0, −1/2). This cation appears to be ordered.

(3) One ordered [GaCl$_4$$^-$] anion, centered on Ga(3), is in a general position with no crystallographic site symmetry.

The gallium−acetylacetonate oxygen distances in the cations are statistically equivalent with an average value of 1.907(6) Å, whereas the gallium−THF oxygen bond distances in cation A and cation B are substantially longer, with values of 2.031(5) and 2.043(5) Å, respectively. The average Ga−O bond distance of 1.907(6) Å associated with the acetylacetonate ligands of the cation is shorter than that of 1.952(6) Å (av) found for the hexacoordinate compound Ga(acac)$_3$.[14] This is most likely a result of the increased charge density on the gallium cationic center compared to the neutral hexacoordinate Ga(acac)$_3$ species. The Ga−O bond distances for the Ga(acac) moiety in the hexacoordinate cation are longer than those observed for the tetracoordinate species GaCl$_2$(acac) of 1.835(9) Å. The Ga−O bond distances for the Ga-acac and Ga-THF moieties are, as expected, each longer by ~0.1 Å than the analogous Al−O distances in [*trans*-Al(acac)$_2$(THF)$_2$$^+$][AlCl$_4$$^-$], 1.845(4) Å (av) for Al−acac and 1.953(4) Å (av) for Al−THF.[7]

The nature of CD$_2$Cl$_2$ solutions of [Ga(bdk)$_2$(THF)$_2$$^+$][GaCl$_4$$^-$] (bdk = acac, tmhd) was investigated by ^{1}H NMR spectroscopy. Even though the room-temperature ^{1}H NMR spectrum of a sample of pure [Ga(acac)$_2$(THF)$_2$$^+$][GaCl$_4$$^-$] was deceptively simple with six resonances, whereas the spectrum of [Ga(tmhd)$_2$(THF)$_2$$^+$][GaCl$_4$$^-$] had eight resonances, multiple species connected by multiple reactions are present in solution. Dissolution of crystals of [*trans*-Ga(bdk)$_2$(THF)$_2$$^+$][GaCl$_4$$^-$] in CD$_2Cl_2$ produces both the trans and cis isomers, the four-coordinate compound GaCl$_2$(bdk), a species that is

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Table 4. ^{1}H NMR Spectral Data for CD_2Cl_2 Solutions of $[Ga(acac)_2(THF)_2^+][GaCl_4^-]^a$

		assignment, δ(ppm)			
compound	*T* (°C)	acac-H	acac-CH_3	OCH_2	RCH_2
$[Ga(acac)_2(THF)_2^+][GaCl_4^-]$	20	5.85a, 5.73	2.22a, 2.14	3.83	1.93
	−40	5.73−5.71br (t+c)	2.14−2.09 br (t+c)	3.74−3.71br (t+c)	1.92−1.89 br, (t+c)
	−80	5.78i, 5.70t 5.62c	2.26i, 2.18i 2.10t, 2.09c, 1.99c	3.92c,3.85c 3.68t	2.06c, 1.94c, 1.88t
$[Ga(acac)_2(THF)_2^+][GaCl_4^-]$ + THF	20	5.73	2.13	3.68	1.81
$GaCl_2(acac)$	20	5.86	2.24		
THF	20			3.68	1.77

[a] a = $GaCl_2(acac)$, c = cis, t = trans, i = intermediate.

Table 5. ^{1}H NMR Spectral Data for CD_2Cl_2 Solutions of $[Ga(tmhd)_2(THF)_2^+][GaCl_4^-]^a$

		assignment,δ(ppm)			
compound	*T* (°C)	bdk-H	tmhd-CH_3	OCH_2	RCH_2
$[Ga(tmhd)_2(THF)_2^+][GaCl_4^-]$	20	6.12a, 5.95 5.76i	1.24a, 1.18br 1.16i	3.93	1.96
	−10	6.12a, 5.95 5.76i	1.24a, 1.18br 1.13	3.93	1.97
	−30	5.88t, 5.80c 5.77i	1.17t+c, 1.10i 1.06br,i, 1.01t	4.07, 3.96 3.68	1.98m,c 1.87i, 1.80t
	-65	5.88t, 5.80c 5.77i	1.17t+c 1.06i, 1.10i, 1.01t	4.05, 3.93 3.68	1.98m, 1.87i, 1.80t
$[Ga(tmhd)_2(THF)_2^+][GaCl_4^-]$ + THF	20	5.94	1.18	3.70	1.83
$GaCl_2(tmhd)$	20	6.12	1.24		

[a] a = $GaCl_2(tmhd)$; c = cis; t = trans; i = intermediate.

observed only at low temperature $[Ga(bdk)_2(THF)^+][GaCl_4^-]$, and free THF. These species were identified by comparing the variable-temperature ^{1}H NMR spectra of $[Ga(bdk)_2(THF)_2^+][GaCl_4^-]$ with the spectra of pure $GaCl_2(bdk)$ and of $[Ga(bdk)_2(THF)_2^+][GaCl_4^-]$ in the presence of excess THF. In addition, signal averaging by a stereochemical rearrangement, a configurational rearrangement of the cis isomer, THF exchange, and the two equilibria represented by eqs 1 and 2 are occurring in solution. The chemical shifts of the resonances observed in the variable-temperature spectra and their assignments are collected in Tables 4 (acac) and 5 (tmhd). When excess THF was present in a solution of $[Ga(bdk)_2(THF)_2^+][GaCl_4^-]$, resonances for $GaCl_2(bdk)$ and $[Ga(bdk)_2(THF)^+][GaCl_4^-]$ were absent. When the temperature of the solution of $[Ga(bdk)_2(THF)_2^+][GaCl_4^-]$ with no excess THF was lowered from 20 °C, the resonances for $GaCl_2(bdk)$ protons decreased in intensity until they were not observed at −30 °C. Upon rewarming, the resonances for $GaCl_2(bdk)$ protons reappeared. Thus, the overall reaction depicted by eq 3 is endothermic. Equilibrium constants for eq 3 were calculated by using the integration values for the unique protons on the bdk ligands. The equilibrium constant at 20 °C for the acac derivative was $(1.1 \pm 0.1) \times 10^{-2}$ and for tmhd was $(8 \pm 1) \times 10^{-3}$. The other thermodynamic parameters calculated from the variable-temperature NMR spectroscopic data for the overall equilibrium involving the acac ligand are $\Delta H° = 17 \pm 1$ kcal/mol, $\Delta S° = 46 \pm 1$ cal/K and for tmhd are $\Delta H° = 17 \pm 1$ kcal/mol, $\Delta S° = 45 \pm 1$ cal/K. It should be noted that the exchange of the THF ligands bonded to the hexacoordinate gallium center with free THF is faster than the exchange of β-diketonate ligands between the tetra- and hexacoordinate species for the gallium compounds.

$$[Ga(bdk)_2(THF)_2^+][GaCl_4^-] \rightleftharpoons [Ga(bdk)_2(THF)^+][GaCl_4^-] + THF \quad (1)$$

$$[Ga(bdk)_2(THF)^+][GaCl_4^-] \rightleftharpoons 2\ GaCl_2(bdk) + THF \quad (2)$$

$$[Ga(bdk)_2(THF)_2^+][GaCl_4^-] \xrightleftharpoons{CD_2Cl_2} 2\ GaCl_2(bdk) + 2\ THF \quad (3)$$

A stereochemical rearrangement of the cis and trans isomers of $[Ga(bdk)_2(THF)_2^+][GaCl_4^-]$ (bdk = acac, tmhd) and a configurational rearrangement of the cis isomer in CD_2Cl_2 were observed by using the ^{1}H NMR spectral data for temperatures below 20 °C, Tables 4 and 5. Spectra for the two compounds were similar, but the temperatures at which significant changes occurred were different. The spectrum of $[Ga(acac)_2(THF)_2^+][GaCl_4^-]$ at −80 °C had resonances that can be attributed to both the trans and cis stereoisomers, as well as to an intermediate such as $[Ga(acac)_2(THF)^+][GaCl_4^-]$, as in aluminum chemistry.[5] A 10:1 ratio of trans to cis stereoisomers was observed by using the integration values for the unique acac-H and the OCH_2 (THF) resonances in the temperature range of −80 to −50 °C, the range where reliable integration values could be obtained. When the temperature of the solution was increased from −80 to −40 °C, the resonances for the protons of the cis isomer broadened and coalesced with each other and with those of the trans isomer as well as with those of the intermediate $[Ga(acac)_2(THF)^+][GaCl_4^-]$. At −40 °C, there was a single set of broad resonances. The resonances for the THF and acac protons had shifted 0.05 and 0.02 ppm, respectively, to lower field in the temperature range of −80 to −30 °C. The temperature dependence of the chemical shifts and intensities of the resonances for the protons of $[Ga(tmhd)_2(THF)_2^+][GaCl_4^-]$ in CD_2Cl_2 solution were simi-

Table 6. Kinetic Parameters for CD_2Cl_2 Solutions of $[Ga(bdk)_2(THF)_2^+][GaCl_4^-]$ and Related Compounds

compound	T_c (K)	$\Delta\nu$ (Hz)	k_c (s^{-1})[a]	$\Delta G^{\ddagger}$ (kcal/mol)[b]	ref
$[Ga(acac)_2(THF)_2^+][GaCl_4^-]_{av}$	233	30.4	67.5	11.6 ± 1.1	
from acac-H		34.4	76.4	11.5 ± 1.0	
from acac-CH_3		26.4	58.6	11.6 ± 1.1	
$[Ga(tmhd)_2(THF)_2^+][GaCl_4^-]_{av}$	263	32.2	71.6	13.3 ± 1.3	
from tmhd-H		31.6	70.2	13.5 ± 1.3	
from tmhd-CH_3		32.8	72.9	13.1 ± 1.2	
$Ga(acac)_2(hfac)$	247	3.35	7.44	13.4[b]	14
$Ga(acac)_2(bzbz)$	354	10.8	23.9	18.9[c]	14
$[Al(acac)_2(THF)_2^+][AlCl_4^-]$	233	8.0	17.8	12.2	17
$[Al(acac)_2(DMF)_2^+][AlCl_4^-]$	268	4.4	9.77	14.4	6

[a] Rate constant at coalescence temperature. [b] $E_a = 14.5 \pm 1.1$ kcal/mol.[14] [c] $E_a = 20.6 \pm 2.7$ kcal/mol.[14]

lar. The spectrum at −65 °C had resonances for the cis and trans stereoisomers and the intermediate $[Ga(tmhd)_2(THF)^+][GaCl_4^-]$. A 3:1 ratio of cis to trans isomers was calculated by using the integration values for the resonances of the tmhd-H protons and the low-field THF resonances. This ratio was constant in the temperature range of −65 to −30 °C. As the temperature of the solution of $[Ga(tmhd)_2(THF)_2^+][GaCl_4^-]$ increased from −65 to −10 °C, the resonances for the symmetrically inequivalent tmhd-CH_3 and the THF protons of the cis isomer broadened and coalesced with each other and concomitantly with the resonances for the trans stereoisomer until single resonances were observed at −10 °C.

The free energies of activation $\Delta G^{\ddagger}$ for the stereochemical rearrangement of $[Ga(bdk)_2(THF)_2^+][GaCl_4^-]$ (bdk = acac, tmhd) were calculated from the variable-temperature ^1H NMR spectral data (Table 6). The average of two calculations of $\Delta G^{\ddagger}$ at the coalescence temperature for each β-diketonate derivative provided $\Delta G^{\ddagger} = 11.6 \pm 1.1$ kcal/mol for the acac ligand and $\Delta G^{\ddagger} = 13.3 \pm 1.3$ kcal/mol for tmhd. The uncertainty in these values of $\Delta G^{\ddagger}$ reflects the uncertainty in the value of T_c (±5 °C). The calculated values of $\Delta G^{\ddagger}$ for each β-diketonate derivative are statistically identical with an average value $\Delta G^{\ddagger}_{av} = 12.5 \pm 1.2$ kcal/mol. Interestingly, this average free energy barrier for stereochemical rearrangement of $[Ga(bdk)_2(THF)_2^+][GaCl_4^-]$ is comparable to that calculated for $Ga(acac)_2(hfac)$,[14] $[Al(acac)_2(THF)_2^+][AlCl_4^-]$,[17] and $[Al(acac)_2(DMF)_2^+][AlCl_4^-]$,[6] but smaller than that for $Ga(acac)_2(bzbz)$[14] (Table 6). The favored pathway for the stereochemical rearrangement of the aluminum compound involved the dissociation of the monodentate Lewis base rather than the dissociation of a carbonyl group of an acetylacetonate ligand, observations consistent with our NMR spectral data. As the activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) for the two compounds were not calculated, further discussion of the mechanism of the rearrangement processes for $[Ga(bdk)_2(THF)_2^+][GaCl_4^-]$ is not warranted.

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 Na(acac),[2,3] Na(tmhd),[2,3] Na(hfac),[2,3] and $Ga(hfac)_3$[13] were prepared by literature methods, whereas $GaCl_3$ and $GaBr_3$ were purchased from Strem Chemicals, Inc. Gallium(III) chloride was vacuum sublimed at 60−80 °C before use, whereas $GaBr_3$ was used as received. 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. ^1H NMR spectra were recorded with either a Varian Unity-Nova 400 or a 500 spectrometer (400 and 500 MHz, respectively), whereas ^{13}C NMR (125.7 MHz) spectra were recorded with the 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 with C_6D_5H at δ 7.15 ppm, the proton impurities in d_8-THF at 1.73 and 3.58 ppm and those of CD_2Cl_2 at 5.32 ppm. Carbon chemical shifts are referenced to $SiMe_4$ at δ 0.00 ppm. All samples for NMR spectra were contained in flame-sealed NMR tubes. Deuterated solvents, benzene-d_6, THF-d_8, and CD_2Cl_2, were purchased from either Aldrich Chemical Co. or Cambridge Isotopes, Inc. Benzene and THF were dried with P_4O_{10} and then vacuum distilled into tubes coated with sodium mirrors. The methylene chloride was dried with only P_4O_{10} and then vacuum distilled at room temperature. Infrared spectra of samples as Nujol mulls between CsI plates were recorded by using a Perkin-Elmer 683 spectrometer. Molecular weights were measured cryoscopically in benzene solution by using an instrument similar to that described by Shriver and Drezdon.[16]

Preparation of $GaCl_2(acac)$. A two-necked flask equipped with a magnetic stir bar and a sidearm dumper that contained 2.51 g (20.6 mmol) of Na(acac) was charged with 3.61 g (20. 5 mmol) of freshly sublimed $GaCl_3$. The two-necked flask was connected in turn to a Schlenk flask by a medium-porosity sintered glass frit. Approximately 50 mL of benzene was vacuum distilled onto the $GaCl_3$. The reaction bulb was warmed to room temperature, and the Na(acac) was added slowly over 20 min to the colorless $GaCl_3$/benzene solution at room temperature. After the reaction mixture had been stirred for 12 h, a colorless solution was separated from a tannish benzene insoluble solid (presumably NaCl) by filtration. The tannish solid was washed once with benzene, and the volatile components were removed by vacuum distillation. The Schlenk flask that contained the benzene-soluble colorless solid was connected to a round-bottomed flask by a clean medium-porosity sintered glass frit. After approximately 30 mL of pentane was added by vacuum distillation, the solid was extracted seven times with filtration. Colorless needles of $GaCl_2(acac)$ formed after placing the bulb that contained the extracted solution in a −30 °C bath for 4 h. This recrystallization process was repeated after each extraction, and 4.30 g (87.8% yield based on $GaCl_3$) of $GaCl_2(acac)$ as colorless needles was collected after removing solvent by vacuum distillation.

$GaCl_2(acac)$: mp 89.6−91.3 °C; soluble in benzene, toluene, CH_2Cl_2, but slightly soluble in pentane. Cryoscopic molecular weight, benzene solution, formula weight 239.74 (observed molality, observed mol wt, association): 0.0667, 264.15, 1.10;

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Table 7. Data for X-ray Crystallographic Studies of $GaCl_2(acac)$, [*trans*-$Ga(acac)_2(THF)_2$][$GaCl_4$], and $GaCl_2(tmhd)$

	$GaCl_2(acac)$	[*trans*-$Ga(acac)_2(THF)_2$][$GaCl_4$]	$GaCl_2(tmhd)$
molec formula	$C_5H_7Cl_2GaO_2$	$C_{18}H_{30}Cl_4Ga_2O_6$	$C_{11}H_{19}Cl_2GaO_2$
M_r	239.7	623.7	323.9
cryst syst	orthorhombic	triclinic	monoclinic
space group	*Imma* (No. 74)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a, Å	7.708(8)	8.986(4)	19.824(8)
b, Å	10.142(11)	9.891(4)	14.599(5)
c, Å	11.899(18)	15.490(9)	12.309(4)
α, deg	90	88.62(4)	90
β, deg	90	86.30(4)	119.50(3)
γ, deg	90	83.35(3)	90
V, Å^3	930(1)	1364.5(11)	3100(2)
D_{calcd}, g/cm^3	1.712	1.518	1.388
Z	4	2	8
μ(Mo Kα), mm^{-1}	3.473	2.390	2.102
T (K)	296	296	297
F(000)	472	632	1328
2θ range, deg	5 to 40	6 to 40	5 to 45
h	−7 to 0	−8 to +8	0 to +21
k	−9 to +9	−9 to +9	−15 to +15
l	−11 to +11	−14 to +14	−13 to +11
no. of reflns collected	973	5073	4187
no. of ind reflns	262	2549	2049
no. of reflns for refinement	188 ($>6\sigma$)	1897 ($>4\sigma$)	1378 ($>6\sigma$)
weighting scheme, w^{-1}	$\sigma^2(F) + 0.0074F^2$	$\sigma^2(F) + 0.0005F^2$	$\sigma^2(F) + 0.0020F^2$
χ(secondary extinction)	not required	0.00027(13)	0.00041(6)
T_{max}/T_{min}	0.2515/0.2321	0.5240/0.4296	0.7589/0.5408
no. of refined params	33	275	149
final R indices[a] (all data)%			
R	6.60	5.71	5.31
R_w	8.80	5.08	5.83
final R indices[a] (obs data) %			
R	4.60	3.95	3.03
R_w	5.89	4.75	4.52
goodness-of-fit	0.80	1.57	0.84
largest, mean Δ/σ	0.002, 0.000	0.040, 0.002	0.002, 0.000
data-to-param ratio	7.9:1	6.9:1	9.2:1
largest diff peak, e Å^{-3}	0.67	0.38	0.26
largest diff hole, e Å^{-3}	−0.48	−0.46	−0.19

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

0.0570, 257.77, 1.08; 0.0339, 254.03, 1.06. Anal. Calcd for $C_5H_7Cl_2GaO_2$: C, 25.05; H, 2.94; Cl, 29.58. Found: C, 24.89; H, 3.19; Cl, 29.75. ^{1}H NMR (500 MHz, C_6D_6, δ): 4.54 (0.6 H, acac-H), 1.20 (6 H, acac-CH_3). ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 5.86 (0.6 H, acac-H), 2.24 (6 H, acac-CH_3). ^{13}C NMR (C_6D_6, δ): 196.99 (C═O), 103.14 (═C−H), 26.88 (acac-CH_3). IR (Nujol mull, C═O/C═C region, cm^{-1}): 1550 (br, vs), 1528 (vs), 1465 (vs), 1362 (s), 1302 (m), 1290 (m), 1255 (m). X-ray quality crystals were grown by vacuum sublimation at 50 °C for 15 h from a sample contained in a glass ampule.

Collection of X-ray Diffraction Data and Structural Solution for $GaCl_2(acac)$. A crystal of size 0.2 × 0.2 × 0.4 mm was sealed into a thin-walled capillary under argon and mounted on a Siemens R3m/V diffractometer. Unit cell parameters were determined as described previously.[18] The Laue symmetry (D_{2h} or mmm) indicated the orthorhombic system. Possible space groups were *Imma* (No. 74) or *Ima*2 (No. 46). The former, centrosymmetric, possibility was chosen and confirmed by the successful solution of the structure in this higher space group. A hemisphere of data (4 equivalent forms) was collected with $2\theta = 5-40°$. Very few reflections were observed above $2\theta = 40°$. Details are given in Table 7.

Calculations were carried out with use of the Siemens SHELXTL PLUS (Release 4.11(VMS)) program package.[19] Analytical scattering factors for neutral atoms[20a] were corrected for the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion.[20b] The molecule lies on a site of *mm* (C_{2v}) symmetry. Hydrogen atoms were located from a difference Fourier synthesis and were optimized with $d(C-H) = 0.96$ Å.[21]

Preparation of [$Ga(acac)_2(THF)_2$][$GaCl_4$]. A 0.236 g (0.983 mmol) sample of $GaCl_2(acac)$ was dissolved in approximately 10−15 mL of THF in a Solv-Seal tube fitted with a vacuum adapter. The resulting solution was allowed to stand for 24 h at room temperature before the excess THF was removed by vacuum distillation. The resulting colorless solid product was placed into a Solv-Seal tube fitted with a vacuum adapter, and approximately 25 mL of benzene was added by vacuum distillation. The quantity of benzene that was added was controlled such that a clear solution was obtained when warmed to 60 °C in an oil bath. After the tube was removed from the oil bath and was allowed to cool slowly to room temperature over a period of 15 h, colorless crystals formed. The mother liquor was decanted from the crystals into a clean Solv-Seal tube in the drybox. The mother liquor was concentrated to about one-fourth its volume by removing benzene by vacuum distillation, and the recrystallization process was repeated. The colorless crystals of [$Ga(acac)_2(THF)_2{}^+$][$GaCl_4{}^-$] were allowed to dry in the drybox for 15 h, and a total of 0.296 g [0.475 mmol, 96.4% yield based on $GaCl_2(acac)$] was collected.

[$Ga(acac)_2(THF)_2$][$GaCl_4$]: mp 119.8−120°C (capillary appeared foggy, possibly due to decomposition by loss of THF);

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(19) Sheldrick, G. M. *SHELXTL PLUS*, Release 4.11 (VMS); Siemens Analytical Instrument Corp.: Madison, WI, 1989.

(20) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, (a) p 99−101; (b) p 149−150.

(21) Churchill, M. R. *Inorg. Chem.* **1973,** *12*, 1213.

140−146 °C (sample liquified and resolidified on cooling). Reheating produced similar results. Soluble in CH_2Cl_2 and THF, slightly soluble in benzene and Et_2O, and very slightly soluble in pentane. Anal. Calcd for $C_{18}H_{30}Cl_4Ga_2O_6$: C, 34.66; H, 4.85; Cl, 22.74. Found: C, 34.82; H, 4.78; Cl, 22.88. IR (Nujol mull, C═O/C═C region, cm^{-1}): 1560 (br, vs), 1480 (vs), 1478, 1465 (vs), 1450, 1427(sh), 1380, 1370, 1360, 1337, 1282 (m), 1195 (m), 1170 (sh), 1017. ^1H NMR (400 MHz, ∼0.1 mM CD_2Cl_2, 20 °C, δ): 5.85 [s, 0.8 H, acac-H, $GaCl_2(acac)$], 5.73 (s,br, 0.7 H, acac-H, $[Ga(acac)_2(THF)_2][GaCl_4]$), 3.83 (m, 4.5 H, THF), 2.22 [s, 6 H, acac-CH_3, $GaCl_2(acac)$], 2.14 (s, br, 6 H, acac-CH_3, $[Ga(acac)_2(THF)_2][GaCl_4]$), 1.94 (m, 4.1 H, THF). ^1H NMR (400 MHz, CD_2Cl_2 + THF, δ): 5.73 (0.7 H, acac-H), 3.68 (m, 17 H, THF), 2.13 (6 H, acac-CH_3), 1.81 (m, 17 H, THF). ^1H NMR (400 MHz, C_6D_6, δ): 4.54 (br, 0.6 H, acac-H), 1.20 (br, 6 H, acac-CH_3).

Collection of X-ray Diffraction Data and Structural Solution for [*trans*-Ga(acac)$_2$(THF)$_2$][GaCl$_4$]. The crystal used was of approximate dimensions 0.46 × 0.30 × 0.18 mm. Crystallographic details are similar to the study on $GaCl_2(acac)$, vide supra. The compound crystallized in the triclinic system; space group $P\bar{1}$ was chosen over the possible $P1$ and proved to be correct. The gallium atoms lie on inversion centers (Ga(1) at 0, 0, 0; Ga(2) at 0, 0, 1/2) which dictates precise C_i symmetry for the two crystallographically independent [*trans*-$Ga(acac)_2(THF)_2^+$] cations. A full sphere of data (2 equivalent forms) was collected with $2\theta = 6-40°$ (the limit of observable data). Details are given in Table 7.

Preparation of GaCl$_2$(tmhd). The title compound was prepared from 1.02 g (6.09 mmol) of freshly sublimed $GaCl_3$, 1.26 g (6.11 mmol) of Na(tmhd), and 30 mL of benzene by using the procedure described for the preparation of $GaCl_2(acac)$. The crude product was isolated by extraction with benzene and was then purified by recrystallization from pentane. Colorless crystalline blocks of $GaCl_2(tmhd)$ formed by cooling a saturated solution at −15 °C bath for 12 h. The recrystallization process gave 1.77 g (6.08 mmol, 90.0% yield based on $GaCl_3$) of $GaCl_2(tmhd)$.

GaCl$_2$(tmhd): mp 106−109 °C; soluble in benzene, toluene and CH_2Cl_2 but slightly soluble in pentane. Anal. Calcd for $C_{11}H_{19}Cl_2GaO_2$: C, 40.79; H, 5.91; Found: C, 40.80; H, 6.19. ^1H NMR (300 MHz, C_6D_6, δ): 5.79 (1.1 H, tmhd-H), 0.86 (18 H, tmhd-CH_3). ^{13}C NMR (75.45 MHz, C_6D_6, δ): 207.84 (C═O), 94.50 (═C−H), 42.33 (ipso-C), 27.74 (tmhd-CH_3). IR (Nujol mull, C═O/C═C region, cm^{-1}): 1590 (sh,m), 1555 (sh,m), 1550 (s), 1542 (vs), 1535 (vs), 1530 (vs), 1522 (vs), 1495(sh,s), 1470 (sh,m), 1455 (vs), 1443 (s), 1393 (w), 1363 (vs), 1330 (vs), 1297 (sh,m), 1247 (m), 1215 (s). X-ray quality crystals were grown by vacuum sublimation at 75−80 °C for 12 h of a sample contained in a glass ampule.

Collection of X-ray Diffraction Data and Structural Solution for GaCl$_2$(tmhd). A crystal of size 0.25 × 0.46 × 0.46 mm was used for the analysis. The crystal belongs to the monoclinic system (2/*m* Laue symmetry). Possible space groups were $C2/c$ (No. 15) and Cc (No. 9). The former, centrosymmetric, possibility was chosen on the basis of intensity statistics and the successful solution of the structure in the higher space group. A hemisphere of data (2 equivalent forms) was collected for $2\theta = 5-45°$ (the limit of observable data). Details are given in Table 7.

Preparation of [Ga(tmhd)$_2$(THF)$_2$][GaCl$_4$]. A 0.493 g (1.52 mmol) sample of $GaCl_2(tmhd)$ was dissolved in approximately 10−15 mL of THF in a Solv-Seal tube fitted with a vacuum adapter as described previously for the acac derivative. The product $[Ga(tmhd)_2(THF)_2][GaCl_4]$ was isolated as a colorless crystalline solid (0.508 g, 84.3% yield) by recrystallization from benzene.

[Ga(tmhd)$_2$(THF)$_2$][GaCl$_4$]: mp 154−157 °C, capillary appeared foggy, possible decomposition by loss of THF; 169−171 °C sample liquified and resolidified on cooling. Reheating the sample produced similar results. Soluble in CH_2Cl_2 and THF, slightly soluble in benzene and Et_2O, and very slightly soluble in pentane. Anal. Calcd for $C_{30}H_{54}Cl_4Ga_2O_6$: C, 45.50; H, 6.87. Found: C, 45.75; H, 7.25. IR (Nujol mull, C═O/C═C region, cm^{-1}): 1613 (w), 1547 (vs), 1510 (vs), 1396 (s), 1372 (sh,m), 1340 (m), 1290 (m), 1248 (m), 1223 (m). ^1H NMR (400 MHz, CD_2Cl_2, 20°C, δ): 6.12 [s, tmhd-H, $GaCl_2(tmhd)$], 5.95 (s, br, $[Ga(tmhd\text{-}H)_2(THF)_2^+]$), 3.93 (br, 4 H, THF), 1.96 (m, 4 H, THF), 1.24 [s, 27% of 18 H, $GaCl_2(tmhd\text{-}CH_3)$], 1.18 [s, br, $[Ga(tmhd\text{-}CH_3)_2(THF)_2^+]$), 1.16 (s, intermediate, see Discussion). ^1H NMR (400 MHz, CD_2Cl_2 + THF, δ): 5.94 (0.8 H, tmhd-H), 3.70 (m, 14 H, THF), 1.82 (m, 17 H, THF), 1.18 (18 H, tmhd-CH_3). ^1H NMR (300 MHz, C_6D_6, δ): 5.80−5.78 (br, 1 H, tmhd-H), 3.72 (br, 4 H, OCH_2), 1.50 (br, 4 H, RCH_2), 1.07 (br, $[Ga(tmhd\text{-}CH_3)_2(THF)_2^+]$), 0.86 $[GaCl_2(tmhd\text{-}CH_3)]$; total integration for tmhd-CH_3 region: 18 H.

Acknowledgment. Purchase of the Siemens R3m/V diffractometer was made possible by Grant No. 89-13733 from the Chemical Instrumentation Program of the National Science Foundation.

Supporting Information Available: (1) Experimental details for the attempted synthesis of $GaX_2(hfac)$ (X = Cl, Br). (2) Complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters and positions for hydrogen atoms, and packing diagrams for the three compounds studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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