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Gallium(II) Compounds Stabilized by *β*-Diketonate Ligands: Synthesis, Characterization, and X-ray Structural Studies of $[GaCl(acac)]_2$ and $[GaCl(tmhd)]_2$

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Two new gallium(II) derivatives, $[GaCl(acac)]_2$ (acac = acetylacetonate and $[GaCl(tmhd)]_2$ (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate), have been prepared and characterized by X-ray structural studies, partial elemental analyses, physical properties, and their ^{1}H NMR, ^{13}C NMR, and IR spectra. Both compounds have direct gallium−gallium bonds between two tetracoordinated gallium atoms with each in the +2 oxidation state and with each gallium bonded to a chloride and a chelated *β*-diketonate ligand. Metal−metal bond lengths are Ga(1)−Ga(1a) = 2.396(3) Å for the acac derivative (which has crystallographically imposed C_2 symmetry) and Ga(1)−Ga(2) = 2.391(2) Å for the tmhd derivative.

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The preparation, characterization, and reactions of low oxidation state gallium compounds[1] with *σ*-bonded ligands other than halogens are of current interest. These types of compounds include derivatives of gallium(I)[2] and gallium(II),[3] as well as species with gallium in undefined oxidation states such as organogallium radicals[2h,4] and gallium clusters.[5] The organogallium(II) compound $Ga_2[CH(SiMe_3)_2]_4$ was prepared by the metathetical reaction between $Ga_2Br_4 \cdot 2diox$ and $LiCH(SiMe_3)_2$ in a 1:4 mol ratio[3a] and has been demonstrated to be a versatile reagent for the preparation of other low oxidation state gallium compounds.[3a,i,j] When a pentane solution of $Ga_2[CH(SiMe_3)_2]_4$ was treated with dibenzoylmethane at −50 °C, $CH_2(SiMe_3)_2$ was eliminated and the gallium(II) *β*-diketonate derivative $\{Ga[CH(SiMe_3)_2](bzbz)]\}_2$[3i] (bzbz = 1,3-diphenyl-1,3-propanedionato) was formed. An X-ray structural study revealed two tetracoordinated gallium centers, each with a chelated *β*-diketonate ligand and with a Ga−Ga bond between them. Our interest in low oxidation state gallium compounds and in studying the effect of the *β*-diketonate ligand on the chemistry of such compounds prompted us to investigate the preparation of the gallium(II) derivatives $[GaCl(acac)]_2$ (acac = acetylacetonate) and $[GaCl(tmhd)]_2$ (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate) by using a reaction that was different from that used to prepare $\{Ga[CH(SiMe_3)_2](bzbz)]\}_2$.[3i]

Results and Discussion

Two gallium(II) *β*-diketonate compounds of the type $[GaCl(bdk)]_2$ (bdk = acac, tmhd) have been prepared by metathetical reactions between $Ga_2Cl_4 \cdot 2THF$ and the appropriate Na(bdk) reagent in a 1:2 mol ratio in THF solution below room temperature (eq 1). The pure

$$\begin{aligned} &Ga_2Cl_4 \cdot 2THF + 2\ Na(bdk) \xrightarrow{THF} \\ &\quad (1-x)\ [GaCl(bdk)]_2 + (2-x)\ THF + 2\ NaCl + \\ &\quad x/2\ [Ga(bdk)_2(THF)_2][GaCl_4] + x/3\ Ga(bdk)_3 + \\ &\qquad 2x/3\ Ga^0 \quad (1) \end{aligned}$$

crystalline compound $[GaCl(acac)]_2$ was isolated in 40% yield, whereas pure $[GaCl(tmhd)]_2$ was isolated in only 24% yield. The relatively low yields of these gallium(II) compounds are due to the formation of numerous gallium(III) side products including $Ga(bdk)_3$, $GaCl_2(bdk)$, $[Ga(bdk)_2(THF)_2][GaCl_4]$, and gallium metal. These products suggest the occurrence of disproportionation

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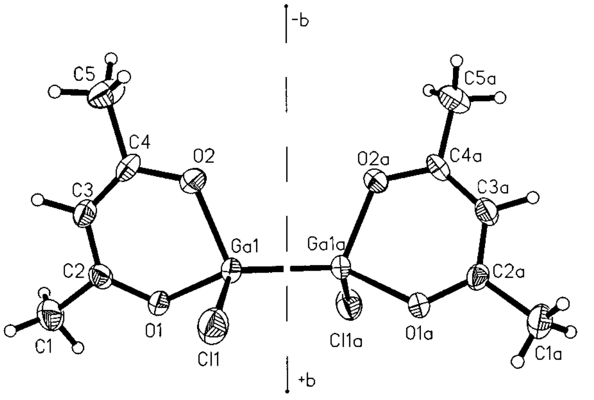

Figure 1. Labeling of atoms in the $[GaCl(acac)]_2$ molecule. The 30% probability envelopes are shown for the vibration ellipsoids of all non-hydrogen atoms, while hydrogen atoms are artificially reduced. The crystallographic 2-fold axis along *b* is indicated by a dashed line.

Table 1. Selected Bond Distances and Angles for $[GaCl(acac)]_2$

Bond Distances (Å)			
Ga(1)−Cl(1)	2.181(3)	Ga(1)−O(1)	1.888(6)
Ga(1)−O(2)	1.889(6)	Ga(1)−Ga(1a)	2.396(3)
O(1)−C(2)	1.277(10)	O(2)−C(4)	1.285(10)
C(1)−C(2)	1.491(13)	C(2)−C(3)	1.378(13)
C(3)−C(4)	1.360(13)	C(4)−C(5)	1.503(14)
Bond Angles (deg)			
Cl(1)−Ga(1)−O(1)	102.3(2)	Cl(1)−Ga(1)−O(2)	104.2(2)
O(1)−Ga(1)−O(2)	95.3(3)	Cl(1)−Ga(1)−Ga(1a)	119.9(1)
O(1)−Ga(1)−Ga(1a)	118.8(2)	O(2)−Ga(1)−Ga(1a)	112.7(2)
Ga(1)−O(1)−C(2)	122.6(6)	Ga(1)−O(2)−C(4)	123.3(6)
O(1)−C(2)−C(1)	115.2(8)	O(1)−C(2)−C(3)	123.9(8)
C(1)−C(2)−C(3)	120.9(8)	C(2)−C(3)−C(4)	127.7(9)
O(2)−C(4)−C(3)	123.3(9)	O(2)−C(4)−C(5)	113.8(8)
C(3)−C(4)−C(5)	122.8(8)		

reactions. The gray color indicative of gallium metal was observed, but only after the THF had been removed from the reaction mixture. The gallium(III) β-diketonate derivatives[6] were identified by their characteristic ^1H NMR spectra. The separation of the gallium(II) compounds from the gallium(III) decomposition products was difficult because the compounds have similar solubilities at room temperature in pentane, benzene, Et_2O, and THF. Repeated fractional crystallizations from hot benzene were used to isolate each of the pure gallium(II) compounds. It is of particular interest that the metathetical reactions were the only successful synthetic routes of those investigated to these gallium(II) β-diketonate compounds. The reaction between Ga_2Cl_4 and H(acac) resulted in the formation of an unidentifiable brown solid rather than $[GaCl(acac)]_2$. Attempts to prepare $[GaCl(bdk)]_2$ (bdk = acac, tmhd) by the reduction of $GaCl_2(bdk)$ by using either sodium metal or sodium naphthalenide in THF solution were also unsuccessful.

The structure of $[GaCl(acac)]_2$ was determined by a single-crystal X-ray structural study. The molecular structure of $[GaCl(acac)]_2$ is depicted in Figure 1, while selected bond distances and angles are collected in Table 1. The molecular geometry reveals the presence of a discrete dimeric species with a direct gallium−gallium bond. The molecule lies on a site of crystallographic C_2 symmetry. The Ga−Ga bond distance in $[GaCl(acac)]_2$ of 2.396(3) Å is shorter than that found for $\{Ga[CH(SiMe_3)_2](bzbz)]\}_2$ [2.440(1) Å][3i] and may be compared with the distances in the gallium(II) compounds $\{Ga[CH(SiMe_3)_2](p\text{-}O_2CC_6H_4Br)\}_2$[3a] (2.385(2) Å), $Ga_2[CH(SiMe_3)_2]_2[1,3\text{-}(Ph)_2N_3]_2$[3a] (2.4579(6) Å), and $\{Ga_2[Si(SiMe_3)_3]_2Cl_2\}_2$[3g] (2.5014(10) and 2.5093(12) Å). Each gallium center has a distorted tetrahedral coordination environment, with the smallest angle about gallium being 95.3(3)° for the O(1)−Ga(1)−O(2) chelate angle and the largest being 119.9(1)° for Cl(1)−Ga(1)−Ga(1a). The acetylacetonate ligand is bonded symmetrically to each gallium center with Ga−O bond distances of 1.888(6) and 1.889(6) Å. These distances are longer than the corresponding Ga−O bond distances for $GaCl_2(acac)$ of 1.835(9) Å,[6] but are shorter than those found for the hexacoordinate gallium(III) species, $Ga(acac)_3$ [av 1.952(6)].[7] The Ga−Cl distance of 2.181(3) Å is comparable with those in other structurally characterized gallium(II) compounds with terminal Ga−Cl bonds such as $Ga_2Cl_4{\cdot}2diox$ (av 2.174(2) Å),[8a] $Ga_2Cl_4{\cdot}2py$ (2.200(2) Å),[8b] and $Ga_2Cl_4{\cdot}2[4\text{-}(Me)py]$ (2.195(2) Å).[8c] The packing diagram for $[GaCl(acac)]_2$ identifies close contacts between the chlorine bound to gallium and hydrogen atoms on the methyl groups of the acac ligand, but these Cl···H−C interactions are relatively weak.

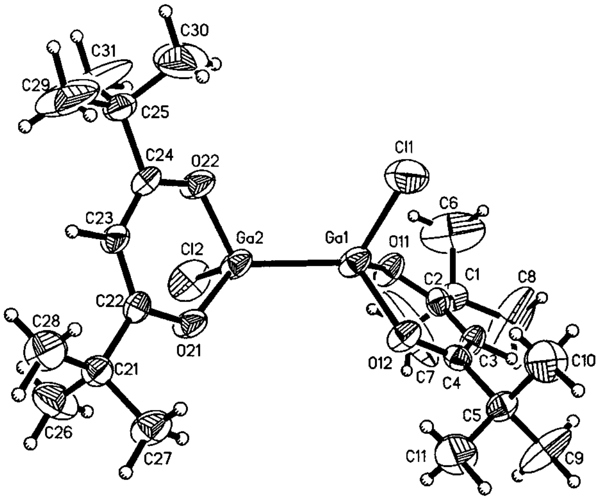

Figure 2. Labeling of atoms in the $[GaCl(tmhd)]_2$ molecule. The 30% probability envelopes are shown for the vibration ellipsoids of all non-hydrogen atoms, while hydrogen atoms are artificially reduced.

The single-crystal X-ray structural study of $[GaCl(tmhd)]_2$ also reveals a discrete dimeric molecule that possesses a gallium−gallium bond with one tmhd ligand and one chloride group bound to each gallium. The structure is depicted in Figure 2. This molecule has no crystallographically imposed symmetry. The relevant bond distances and angles are collected in Table 2. The Ga(1)−Ga(2) distance of 2.391(2) Å is statistically indistinguishable from that of 2.396(3) Å found for $[GaCl(acac)]_2$. Each of the gallium centers has a distorted tetrahedral coordination geometry, with the

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Table 2. Selected Bond Distances and Angles for $[GaCl(tmhd)]_2$

Bond Distances (Å)			
Ga(1)−Ga(2)	2.391 (2)	Ga(1)−Cl(1)	2.176 (3)
Ga(1)−O(11)	1.890 (5)	Ga(1)−O(12)	1.886 (5)
Ga(2)−Cl(2)	2.167 (3)	Ga(2)−O(21)	1.879 (5)
Ga(2)−O(22)	1.879 (5)	O(11)−C(2)	1.286 (8)
O(12)−C(4)	1.286 (8)	O(21)−C(22)	1.280 (8)
O(22)−C(24)	1.279 (9)	C(22)−C(23)	1.373 (10)
C(2)−C(3)	1.368 (10)	C(23)−C(24)	1.381 (11)
C(3)−C(4)	1.372 (10)		
Bond Angles (deg)			
Ga(2)−Ga(1)−Cl(1)	117.8(1)	Ga(2)−Ga(1)−O(11)	114.3(1)
Cl(1)−Ga(1)−O(11)	106.3(2)	Ga(2)−Ga(1)−O(12)	119.3(1)
Cl(1)−Ga(1)−O(12)	101.3(2)	O(11)−Ga(1)−O(12)	94.5(2)
Ga(1)−Ga(2)−Cl(2)	118.5(1)	Ga(1)−Ga(2)−O(21)	117.8(1)
Cl(2)−Ga(2)−O(21)	104.1(2)	Ga(1)−Ga(2)−O(22)	112.4(2)
Cl(2)−Ga(2)−O(22)	105.4(2)	O(21)−Ga(2)−O(22)	95.7(2)

chelate angles (O(11)−Ga(1)−O(12) = 94.5(2)° and O(21)−Ga(1)−O(22) = 95.7(2)°) being the smallest angles about gallium. Each of the β-diketonate ligands is bound to gallium in a symmetrical, bidentate manner. The Ga-tmhd moieties are associated with Ga−O distances that range from 1.890(5) Å for Ga(1)−O(11) down to 1.879(5) Å for Ga(2)−O(21) and Ga(2)−O(22), averaging 1.884(5) Å. These distances are similar to those in $[GaCl(acac)]_2$ (vide supra) but are significantly longer than the Ga−O distances of 1.849(4) and 1.841(3) Å found for $GaCl_2(tmhd)$.[6] The two independent Ga−Cl bond distances within the $[GaCl(tmhd)]_2$ molecule are Ga(1)−Cl(1) = 2.176(3) Å and Ga(2)−Cl(2) = 2.167(3) Å. These distances are not distinguishable from their average value of 2.172(5) Å and may be compared with the single independent Ga−Cl distance of 2.181(3) Å found for $[GaCl(acac)]_2$ and the range of 2.165(2)−2.182(2) Å found for the Ga−Cl bonds in $Ga_2Cl_4{\cdot}2diox$.[8a]

The compounds $[GaCl(bdk)]_2$ (bdk = acac, tmhd) have some interesting chemical properties. Both gallium(II) β-diketonate derivatives are thermally stable at room temperature but are sensitive to oxidation and hydrolysis. They are best stored as the crystalline solids either under an inert atmosphere or under vacuum. The β-diketonate ligands appear to enhance the thermal stability of the gallium(II) derivative when compared with the halogenated gallium(II) compounds, $Ga_2Cl_4{\cdot}2diox$ and $Ga_2Cl_4{\cdot}2THF$. When $[GaCl(acac)]_2$, $[GaCl(tmhd)]_2$, $Ga_2Cl_4{\cdot}2diox$, and $Ga_2Cl_4{\cdot}2THF$ were heated slowly at approximately the same rate (power level 4.2 on a Mel-Temp 2 apparatus), the decomposition temperatures were observed to be 129−132 °C for $[GaCl(acac)]_2$, 115−120 °C for $[GaCl(tmhd)]_2$, but 80−90 °C for both $Ga_2Cl_4{\cdot}2THF$ and $Ga_2Cl_4{\cdot}2diox$. Even though both $[GaCl(acac)]_2$ and $[GaCl(tmhd)]_2$ are thermally stable as solids at room temperature, C_6D_6 solutions, which were contained in flame-sealed NMR tubes, underwent disproportionation reactions. Gallium metal was observed as a black powder in 2−3 days, whereas the presence of the two gallium(III) β-diketonate species $GaCl_2(bdk)$ and $Ga(bdk)_3$ were identified by their characteristic lines in their ^1H NMR spectra. Furthermore, disproportionation of $[GaCl(acac)]_2$ to gallium metal and gallium(III) acetylacetonate species appears to take place faster in THF than in benzene solution. Within 5 min of dissolving pure $[GaCl(acac)]_2$ in THF-d_8, gallium metal was observed. The ^1H NMR spectrum of the resulting solution had many resonances indicative of β-diketonate protons, but only those resonances at 5.36 and 1.82 ppm for $Ga(acac)_3$ protons could be identified. After 7 h at room temperature, the resonances for $Ga(acac)_3$ had increased in intensity whereas the unassigned resonances had decreased. The chemical shifts of the unassigned resonances were not consistent with the presence of either $GaCl_2(acac)$ or $[Ga(acac)_2(THF)_2{}^+][GaCl_4{}^-]$.[6]

The spectroscopic data for the pure compounds $[GaCl(bdk)]_2$ (bdk = acac, tmhd) indicate that the β-diketonate moieties act as symmetrical, chelating ligands as identified in their solid-state structures. The ^1H and ^{13}C NMR spectra for benzene solutions of $[GaCl(bdk)]_2$ had only one set of resonances associated with the appropriate β-diketonate ligand. Since these gallium(II) β-diketonate derivatives have approximate C_2 symmetry, two sets of resonances due to the possible existence of stereoisomers would be expected. However, the ^1H NMR spectrum of $[GaCl(bdk)]_2$ may be accounted for if either a rapid dissociative reaction at one of the carbonyl groups of the bdk ligands occurred in solution or the resonances for the bdk protons of each stereoisomer were coincidentally superimposed. The simple NMR spectra of $[GaCl(bdk)]_2$ and the propensity of these compounds to disproportionate are indicative of rapid rearrangements of $[GaCl(bdk)]_2$. Variable-temperature ^1H NMR studies of the gallium(II) β-diketonates were not investigated due to their low solubility in aromatic solvents and to the occurrence of disproportionation reactions in both CD_2Cl_2 and THF. Finally, the IR spectrum of $[GaCl(acac)]_2$ had a broad absorption centered at 1550 cm^{-1} for the C−O stretching vibration, whereas the spectrum of $[GaCl(tmhd)]_2$ exhibited absorptions centered at 1547 cm^{-1} for the C−O stretching vibration. These C−O stretching frequencies were lower in energy than those found for the gallium(III) derivatives of the type $GaR_2(bdk)$[9] (typically 1575−1610 cm^{-1}) but were similar to those observed for the closely related $GaCl_2(bdk)$ derivatives (1550 cm^{-1}).[6]

Experimental Section

All compounds described in this investigation were exceedingly 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. Since our experimental observations suggested that the low oxidation state gallium compounds were exceedingly sensitive to decomposition to gallium metal, all glassware and solvents were handled with special precautions. Full details are provided. Dow Corning High-Vacuum Silicone grease that is used for the lubrication of ground-glass joints of glassware is believed to initiate the decomposition, possibly disproportionation, of the gallium(II) compounds. Therefore, most, but not all, of the successful preparations of low-valent gallium compounds were performed by utilizing Solv-Seal glassware without silicone grease. All glassware, after cleaning with alcoholic KOH, nitric acid, distilled water, and acetone, received a final rinse with either benzene or hexanes followed by acetone to remove any silicone grease which might coat the surface of the glassware. All glassware was dried in a 160 °C oven for a minimum of 12 h. All solvents were carefully dried using special precautions. Benzene, toluene, Et_2O, THF, and

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dioxane were refluxed over sodium benzophenone until the solution was violet or red-violet in color. In those cases in which the solvents were refluxed over sodium benzophenone but the ketyl was only deep blue rather than violet, immediate formation of gallium metal was observed upon introduction of the solvent to the low oxidation state precursor. Benzene and toluene were vacuum distilled from the ketyl onto P_4O_{10} and then stirred for a minimum of 12 h before transfer by vacuum distillation to storage bulbs which contained freshly prepared sodium mirrors. Diethyl ether, THF, and dioxane were transferred by vacuum distillation from the ketyl to storage bulbs that contained freshly made sodium mirrors. All of the aforementioned solvents were then vacuum distilled into storage bulbs that contained benzophenone and freshly cut sodium. Then, the solvent was warmed by using a hot water bath and agitated until the solution became violet. Pentane was refluxed over calcium hydride for 3 days before being transferred by vacuum distillation to a storage bulb with a freshly prepared sodium mirror. Meticulous attention must be paid to all of the details in the following experimental procedures. Deviations from the previously described procedures for cleaning glassware and drying solvents, the presence of residual grease on glassware and in the vacuum line, shorter evacuation times, larger quantities of solvent, faster rates of warming of reaction mixtures, and longer reaction times resulted in the formation of a mixture of the desired product and gallium metal and gallium(III) species, products of disproportionation**.** The starting gallium compound Ga_2Cl_4 was either purchased from Strem Chemicals, Inc. and used after the purity was checked by comparing its melting point with the literature (mp: 173.7−175.4 °C, lit.[10] 172 °C) or prepared from freshly sublimed $GaCl_3$ and gallium metal (ca. 1.95:1 mol ratio) in dry benzene.[10] When Solv-Seal glassware was used for a preparative reaction, the typical yield of $Ga_2Cl_4$was 90−95% based on the gallium(III) halide. The β-diketonate reagents Na(acac) and Na(tmhd) were prepared by reacting an excess of the diketone with NaH in pentane at room temperature. Then, after all volatile material had been removed by vacuum distillation, the resulting solid was washed with pentane and finally dried under vacuum. 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 samples as Nujol mulls between CsI plates were recorded by using a Perkin-Elmer 683 spectrometer. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.45 MHz) spectra were recorded with a Varian Gemini 300 spectrometer. Proton chemical shifts are reported in δ (ppm) units and are referenced to $SiMe_4$ at δ 0.00 ppm and either C_6D_5H at δ 7.15 or the proton impurities in THF-d_8 at δ 3.58 and 1.73 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.

Preparation of Ga_2Cl_4·2THF. A round-bottomed Solv-Seal flask fitted with a magnetic stir bar and a vacuum adapter was charged with 0.612 g (2.18 mmol) of Ga_2Cl_4. After the apparatus had been attached to the manifold section of the vacuum line nearest to the diffusion pump, the valves between the vacuum line and reaction flask were evacuated for a minimum of 20 min. Then, the apparatus was evacuated for no less than 30 min. Finally, approximately 1.2 mL of THF (15 mmol) contained in a small tube with freshly cut sodium was vacuum distilled at room temperature onto the Ga_2Cl_4 held at −196 °C. After addition of the THF, the material in the reaction flask was partly colorless and partly yellow. Then the reaction flask was transferred immediately to a small dewar that contained a −78 °C (dry ice−2-propanol) bath. Upon warming from −196 to −78 °C, the reaction mixture contained a solid beneath an intensely yellow solution. When the reaction mixture had been stirred for 15 h, during which time the −78 °C bath had warmed to room temperature, a colorless solution formed. Finally, the volatile components of the reaction mixture were removed by vacuum distillation to leave 0.845 g (91.2% yield) of Ga_2Cl_4·2THF as a colorless solid. It should be noted that the bright yellow color of the reaction mixture begins to dissipate as the reaction mixture reaches approximately −30 °C. The yellow color typically disappeared within 30 min of warming to −30 °C. However, removal of the solvent by vacuum distillation soon after the reaction mixture became a colorless solution yielded the best results. Isolation of Ga_2Cl_4·2THF prior to subsequent reactions is not necessary. However, immediate use of the colorless solution gave the best results because THF solutions of Ga_2Cl_4·2THF slowly decompose to gallium metal. Ga_2Cl_4·2THF: mp 85.3−86.8 °C (dec to colorless liquid and gallium metal).

Preparation of [GaCl(acac)]$_2$. A two-necked flask equipped with a magnetic stir bar and a sidearm dumper that contained 0.592 g (4.85 mmol) of Na(acac) was charged with 0.680 g (2.42 mmol) of Ga_2Cl_4 (Strem Chemicals, Inc.). The reaction flask was then connected to the manifold section of the vacuum line nearest to the diffusion pump, and the valves between the vacuum line and flask were evacuated for 30 min. After the reaction flask was evacuated for a minimum of 20 min, approximately 20 mL of THF at room temperature was vacuum distilled onto the Ga_2Cl_4 held at −196 °C. Upon the addition of THF, the reaction mixture was partly yellow and partly red-brown. The reaction flask was immediately transferred from the liquid nitrogen bath to a dewar that contained a −78 °C bath. The reaction mixture was then noted to consist of a solid beneath a bright yellow solution. After the reaction mixture had been stirred for 12 h and the −78 °C bath had warmed to 5 °C, the reaction mixture was a colorless solution. The reaction bulb was transferred to a dewar that contained a −20 °C bath, and the Na(acac) was added over a period of 5 min. After the reaction mixture had been stirred for an additional 5 h, the THF was removed by vacuum distillation at room temperature to provide a glassy, colorless solid. In the drybox, the two-necked flask was connected to a Schlenk flask by a medium-porosity glass frit. Next, approximately 25 mL of Et_2O was added by vacuum distillation and the Et_2O-soluble portion of the product mixture was separated by filtration (9 extractions) from the gray Et_2O-insoluble portion (presumably NaCl, unreacted Na(acac), and gallium metal). The Et_2O was removed by vacuum distillation at room temperature to provide 0.836 g of a colorless, slightly Et_2O-soluble solid that was identified after examination of its ^{1}H NMR spectrum as a mixture of possibly [GaCl(acac)]$_2$, Ga(acac)$_3$, GaCl$_2$(acac), and [Ga(acac)$_2$(THF)$_2$][GaCl$_4$].[6] The gray Et_2O-insoluble solid was discarded. The impure [GaCl(acac)]$_2$ was placed into a Solv-Seal tube that was fitted with a vacuum adapter, and 20 mL of benzene was added by vacuum distillation at room temperature. The tube was then placed in an 80 °C oil bath and was agitated until dissolution occurred. The tube was removed from the oil bath and was allowed to cool slowly to room temperature. After 14 h, colorless crystalline plates of pure [GaCl(acac)]$_2$ were observed beneath a colorless solution. In the drybox, the mother liquor was decanted from the colorless crystalline plates into a clean Solv-Seal tube and the colorless crystalline plates were allowed to dry for 15 h. The tube that contained the mother liquor was removed from the drybox and the volume of the solution was reduced to approximately 10−15 mL by room-temperature vacuum distillation. The resulting saturated solution was placed again in the 80 °C oil bath and agitated until dissolution. The solution was cooled to room temperature, and a second batch of colorless crystals was collected as described above. A total of 0.390 g (39.5% based on Ga_2Cl_4) of pure [GaCl(acac)]$_2$ as colorless crystalline plates was collected. Similar results were obtained when [GaCl(acac)]$_2$ was prepared by reacting pre-

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[10] Beamish, J. C.; Wilkinson, M.; Worrall, I. J. *Inorg. Chem*. **1978**, *17*, 2026.

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formed Ga_2Cl_4·2THF with Na(acac) by using the above procedure. $[GaCl(acac)]_2$: mp 129−132 °C dec to a gray metallic material (possibly gallium metal) and a colorless liquid. Solubility: THF (soluble) > Et_2O (slightly soluble) ≈ benzene (slightly soluble) ≫ pentane (insoluble); decomposes immediately in CH_2Cl_2. Anal. Calcd for $C_{10}H_{14}Cl_2Ga_2O_4$: C, 29.40; H, 3.45. Found: C, 29.42; H, 3.64. ^1H NMR (C_6D_6,δ): 4.80 (1 H, acac-H), 1.40 (6 H, acac-CH_3). ^{13}C NMR (C_6D_6, δ): 194.99 (C═O), 102.79 (═C-), 27.20 (−CH_3). IR (Nujol, cm^{-1}) (C═C, C═O): 1565 (sh, s), 1560 (sh, s), 1555 (sh, s), 1550 (vs), 1532 (vs), 1528 (vs), 1455 (s), 1450 (sh, vs), 1360 (s), 1339 (vs), 1282 (m). ^1H NMR (initial product mixture before purification, C_6D_6 δ) [assignment, % composition]: 5.15, 1.74 [$Ga(acac)_3$, 12.4%]; 4.96, 1.58 {$[Ga(acac)_2(THF)_2][GaCl_4]$, 10.2%}; 4.80, 1.40 {$[GaCl(acac)]_2$, 68.3%); 4.56, 1.22 [$GaCl_2(acac)$, 9.1%]. The proposed assignments for the lines observed in the above spectrum are based on comparisons between the observed chemical shifts and those found for pure species prepared independently.[6] Percent composition of a species is based on integration of ^1H NMR spectra. The total recoverable yield of pure $[GaCl(acac)]_2$ of 62.0% was suggested by both mass determination and the NMR spectrum of the crude product. ^1H NMR (THF-d_8, δ) 5 min after dissolving pure $[GaCl(acac)]_2$ in THF, trace gallium metal observed: *acac-H region:* 5.80 (br), 5.76, 5.66, 5.63, 5.55, 5.36 [$Ga(acac)_3$], *acac-CH₃ region:* 2.10 (br), 2.09, 2.06, 2.04, 2.03, 1.98, 1.86 [$Ga(acac)_3$]. ^1H NMR (THF-d_8, δ) 7 h after dissolving pure $[GaCl(acac)]_2$ in THF, gallium metal observed: *acac-H region:* 5.82, 5.77, 5.75, 5.67, 5.64, 5.57, 5.54, 5.36 [$Ga(acac)_3$], *acac-CH₃ region:* 2.12, 2.091, 2.086, 2.08, 2.07, 2.04, 2.03, 2.00, 1.87 [$Ga(acac)_3$].

Preparation of $[GaCl(tmhd)]_2$. A Solv-Seal two-necked flask fitted with a vacuum adapter, magnetic stir bar, and a sidearm dumper that contained 1.527 g (7.403 mmol) of Na(tmhd) was charged with 1.036 g (3.683 mmol) of Ga_2Cl_4. The solvent THF (20 mL) was introduced by using a procedure that was identical with that described previously for the preparation of $[GaCl(acac)]_2$. The reaction mixture became yellow upon the addition of THF at −196 °C. The reaction flask was transferred immediately to a dewar that contained a −78 °C bath (dry ice−2-propanol), and the reaction mixture was observed to change to a solid beneath a bright yellow solution. After the reaction mixture had been stirred 6 h, the temperature of the bath was −30 °C, and the reaction mixture was a colorless solution. The reaction flask was transferred to another dewar that contained a −78 °C bath, and the reaction mixture was stirred for 30 min before the Na(tmhd) was added over a period of 5 min. After the reaction mixture had been stirred for 15 h and the −78 °C bath had warmed to room temperature, a colorless solid was observed beneath a colorless solution. The THF was removed by vacuum distillation to leave a glassy, colorless solid. In the drybox, the two-necked flask was connected to a Schlenk flask by a medium-porosity sintered glass frit. Next, approximately 30 mL of benzene and 20 mL of pentane were added to the product mixture by vacuum distillation. After filtration, the volatile components were removed by vacuum distillation at room temperature to provide 2.049 g of a mixture of possibly $[GaCl(tmhd)]_2$, $GaCl_2(tmhd)$, $[Ga(tmhd)_2(THF)_2][GaCl_4]$, and $Ga(tmhd)_3$ (determined by its ^1H NMR spectrum) as a benzene/pentane-soluble colorless solid. The light gray, insoluble solid (presumably NaCl, unreacted Na(tmhd), and gallium metal) was discarded. In the drybox, the impure $[GaCl(tmhd)]_2$ was transferred to a Schlenk flask that had been connected to a round-bottomed flask by a sintered glass frit. Approximately 25 mL of pentane was added by vacuum distillation, and the resulting saturated solution was placed in a recirculating bath maintained at −15 °C. After 3 h, colorless crystalline plates were observed beneath the colorless solution. The mother liquor was separated from the colorless crystalline plates by filtration, and then the solvent was removed by vacuum distillation. After three such extractions with subsequent removal of the solvent, a total of 0.5051 g (23.8%) of pure $[GaCl(tmhd)]_2$ was collected as a colorless crystalline solid in approximately 0.1−0.2 g crops. $[GaCl(tmhd)]_2$: mp 114−117 °C dec to a gray metallic material (possibly gallium metal) and a colorless liquid. Anal. Calcd for $C_{22}H_{38}Cl_2Ga_2O_4$: C, 45.80; H, 6.64. Found: C, 46.04; H, 7.04. ^1H NMR (recrystallized product, C_6D_6 δ): 5.85 (1.1 H, tmhd-H), 0.98 (18 H, tmhd-CH_3). ^{13}C NMR (C_6D_6,δ): 205.26 (C═O), 93.68 (−C═), 41.99 (*ipso* −C), 27.95 (−CH_3). IR (Nujol, cm^{-1}) (C═C, C═O region): 1612 (w), 1573 (sh, m), 1569 (sh, m), 1555 (sh, s), 1547 (vs), 1531 (vs), 1525 (vs), 1463 (s), 1450 (sh, s), 1390 (sh, m), 1360 (vs), 1347 (vs), 1292 (m), 1247 (s), 1227 (s). ^1H NMR (initial product mixture, C_6D_6 δ): tmhd-H region: 5.87 ($[Ga(tmhd)_2(THF)_2][GaCl_4]$), 5.85 ($[GaCl(tmhd)]_2$), 5.82 ($Ga(tmhd)_3$), 5.76 ($GaCl_2(tmhd)$); tmhd-$CH_3$ region: 1.20 ($Ga(tmhd)_3$), 1.16, 1.11, 1.06 ($[Ga(tmhd)_2(THF)_2][GaCl_4]$), 0.98 ($[GaCl(tmhd)]_2$), ($GaCl_2(tmhd)$). The proposed assignments for the lines observed in the spectrum of the initial product are based on comparisons between the observed chemical shifts and those found for pure species prepared independently.[6]

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

	$[GaCl(acac)]_2$	$[GaCl(tmhd)]_2$
molec formula	$C_{10}H_{14}Cl_2Ga_2O_4$	$C_{22}H_{38}Cl_2Ga_2O_4$
M_r	408.6	576.9
cryst syst	orthorhombic	monoclinic
space group	*Pbcn* (No. 60)	$P2_1/n$ (No. 14, var)
a, Å	15.756(11)	10.473(5)
b, Å	7.598(4)	9.334(3)
c, Å	12.815(8)	29.895(14)
β, deg	90.000	98.50(4)
V, $Å^3$	1534.0(17)	2890(2)
D_{calcd}, g/cm^3	1.769	1.326
Z	4 (dimeric units)	4 (dimeric units)
μ(Mo Kα), mm^{-1}	3.854	2.065
T (K)	298	297
scan mode	$2\theta-\theta$	ω
2θ range, deg	6.0−45.0	5.0−45.0
h	−16 to 0	0 to 11
k	0 to 8	0 to 10
l	−13 to 0	−32 to 31
no. of reflns collected	1203	4284
no. of reflns used for refinement	691	2059
abs corr	not necessary	Ψ-scans
T_{min}/T_{max}	N/A	0.3675/0.4295
no. of refined params	85	278
final *R* indices (all data)[a]	$R = 7.01\%$ $R_w = 6.26\%$	$R = 8.67\%$ $R_w = 4.74\%$
final *R* indices (obs data)[a]	$R = 4.37\%$ $R_w = 5.53\%$ $(\lvert F_o\rvert > 4\sigma(F_o)$	$R = 4.00\%$ $R_w = 4.05$ $(\lvert F_o\rvert > 6\sigma(F_o))$
largest diff peak, e $Å^{-3}$	0.75	0.42
largest diff hole, e $Å^{-3}$	−0.44	−0.26

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

X-ray Diffraction Studies. Collection of X-ray Diffraction Data, and Structural Solution for $[GaCl(acac)]_2$. A colorless and almost equidimensional crystal (0.4 × 0.35 × 0.3 mm) was sealed into a glass capillary and mounted on a Siemens R3m/V diffractometer. The crystal's Laue symmetry (*mmm*), crystal class (orthorhombic), orientation matrix, and cell dimensions were determined as described previously.[11] Details are provided in Table 3.

Data were corrected for *Lp* factors but not for absorption (Ψ-scans were subject to fluctations of the same order as the errors associated with counting statistics). The systematic absences ($0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, $hk0$ for $h + k = 2n + 1$) uniquely define the space group *Pbcn*.[12]

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(11) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

(12) *International Tables for X-ray Crystallography*, 2nd ed.; Kynoch Press: Birmingham, England, 1965; Vol. 1, p 149.

Crystallographic computations were carried out with the use of the SHELXTL PLUS (Release 4.11(VMS)) program package.[13] The analytical neutral atom scattering factors were corrected for both real and imaginary components of anomalous dispersion.[14] The structure was solved by a combination of Patterson synthesis, difference Fourier syntheses, and least-squares refinement. The molecule lies on a crystallographic 2-fold axis. All non-hydrogen atoms were located and refined anistropically. Hydrogen atoms were located and included in idealized positions based on $d(\mathrm{C-H}) = 0.96$ Å.[15] Their thermal parameters were refined (with those of the two methyl substituents refined as a single parameter). The final discrepancy index was $R = 4.37\%$ for those reflections with $|F_o| > 4\sigma(|F_o|)$.

Collection of X-ray Diffraction Data and Structural Solution for [GaCl(tmhd)]$_2$. An opaque white crystal of dimensions 0.31 × 0.43 × 0.52 mm was sealed into a glass capillary. The procedure paralleled that for the previous structural study, and details are provided in Table 3. Points of interest include the following: (1) The systematic absences ($h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$) and the Laue symmetry ($2/m$) indicate the monoclinic space group $P2_1/n$. (2) The molecule lies in a general position and has no crystallographically imposed symmetry. (3) A total of 4284 reflections were collected, corrected for Lp factors and absorption, and merged ($R_{\mathrm{int}} = 0.78\%$) to a set of 3754 unique data of which 2059 were considered "observed" with $|F_o| > 6\sigma(F_o)$. (4) The structure was solved by direct methods and refined to $R = 4.00\%$ for the "observed" data.

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

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

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99−101 and 149−150.

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

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