Diorganogallium *β*-Diketonates and Their Lewis Acid−Base Adducts. Crystal and Molecular Structures of $Mes_2Ga(hfac)$ and $Me_2Ga(hfac)\cdot NC_5H_5$

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Received November 12, 1997

Compounds of the type $R_2Ga(bdk)$ (R = Me, Et, Mes (mesityl); bdk = 2,4-pentanedionato (acac), 1,1,1-trifluoro-2,4-pentanedionato (tfac), 1,1,1,5,5,5-hexafluoro-2,4-penatedionato (hfac), 2,2,6,6-tetramethyl-3,5-heptanedionato (tmhd)) have been prepared by multiple routes, including hydrocarbon elimination, metathesis, and ligand redistribution reactions, and fully characterized by elemental analyses, cryoscopic molecular weight studies in benzene, and IR and multinuclear NMR spectroscopic studies. An X-ray structural study of Mes_2Ga(hfac) demonstrated four-coordinate gallium with σ bonds to the two mesityl rings and to the two oxygen atoms of the *β*-diketonate ligand. The Lewis acidities of the diorganogallium *β*-diketonate derivatives toward NMe_3 and/or pyridine were also investigated. Two adducts, $Me_2Ga(hfac)\cdot NMe$ and $Me_2Ga(hfac)\cdot py$, were stable to dissociation at room temperature and thus were fully characterized by elemental analysis, cryoscopic molecular weight studies in benzene, vapor pressure−temperature studies, and IR and multinuclear NMR (including variable temperature) spectroscopic studies. The compound $Me_2Ga(hfac)\cdot py$ was also characterized by an X-ray structural study. The structure involved five-coordinate gallium with one Ga−N, two (inequivalent) Ga−O, and two Ga−C bonds.

The incorporation of ligands with potential for the intramolecular stabilization of group 13 compounds in order to reduce their reactivity toward nucleophilic reagents and ligand redistribution reactions is of current interest.[1] Therefore, an investigation of the chemistry of organogallium compounds with *β*-diketonate ligands which are uninegative, symmetrical and potentially bidentate was initiated. Even though an extensive literature exists on the chemistry of diorganoaluminum[2] and diorganoindium[3] *β*-diketonate derivatives, the corresponding gallium compounds have been little explored. Coates and Hayter[4] reported in 1953 the preparation of the first diorganogallium *β*-diketonate derivative $Me_2Ga(acac)$ by a direct reaction between trimethylgallium and acetylacetone, while the second example, $Et_2Ga(acac)$,[5] was not described until 1991. Sato, Yamada, and Sugiura[5] noted the increased air and pyrolytic stability of $Et_2Ga(acac)$ as compared to triethylgallium. As the first part of our investigation into the nature of gallium *β*-diketonate compounds, we report on the preparation of a series of diorganogallium *β*-diketonates by multiple types of reactions. These compounds were used then to investigate the effects of the *β*-diketonate ligand and of the organic groups bound to gallium on their physical and chemical properties, including Lewis acidity.

The twelve diorganogallium *β*-diketonate compounds $R_2Ga(bdk)$ (R = Me, Et, Mes; bdk = hfac, tfac, acac, tmhd) have been prepared in high yield by one or more of three different types of synthetic reactions: elimination reactions, metathesis reactions and ligand redistribution reactions. The elimination reaction (eq 1) was

$$GaR_3 + H(bdk) \rightarrow R_2Ga(bdk) + RH \qquad (1)$$

$$R_2GaCl + Na(bdk) \rightarrow R_2Ga(bdk) + NaCl \qquad (2)$$

$$2GaR_3 + Ga(bdk)_3 \rightarrow 3R_2Ga(bdk) \qquad (3)$$

the most desirable because nearly quantitative yields of easily separable products were obtained in one synthetic step from the readily available reagents. Metathesis reactions (eq 2) were also used to synthesize pure products in high yields. However, this reaction in comparison with the elimination reaction suffers the disadvantage that additional synthetic steps are required for the preparation of the reagents. A stoichiometric ligand redistribution reaction (eq 3) is the least desirable. This method suffers the same type of disad-

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S0276-7333(97)00988-6 CCC: $15.00
Publication on Web 02/20/1998

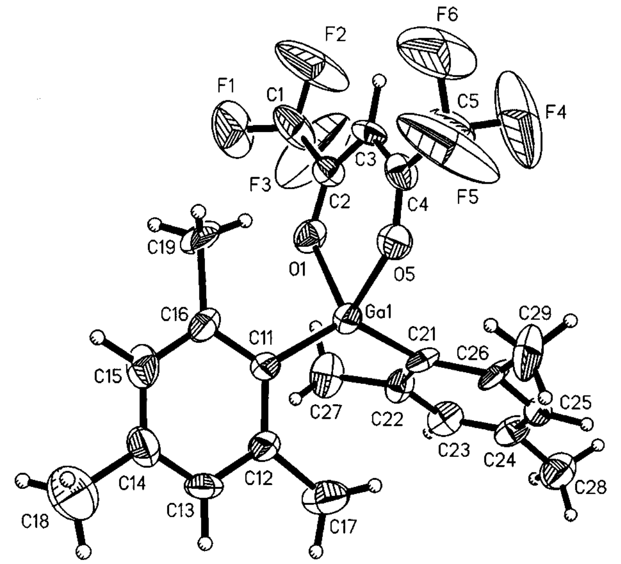

Figure 1. Molecular geometry of $Mes_2Ga(hfac)$ (ORTEP2 diagram, 30% probability envelopes for thermal vibration ellipsoids, with hydrogen atoms artificially reduced).

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $Mes_2Ga(hfac)$

(a) Gallium−Ligand Bond Lengths			
Ga(1)−O(1)	2.008(11)	Ga(1)−C(11)	1.971(13)
Ga(1)−O(5)	2.009(11)	Ga(1)−C(21)	1.943(10)
(b) Bond Lengths within Chelate Ring			
O(1)−C(2)	1.245(20)	C(2)−C(3)	1.392(24)
O(5)−C(4)	1.252(21)	C(3)−C(4)	1.422(23)
(c) Bond Lengths Involving CF_3 Groups			
C(1)−F(1)	1.18(3)	C(5)−F(4)	1.26(4)
C(1)−F(2)	1.21(3)	C(5)−F(5)	1.26(3)
C(1)−F(3)	1.30(3)	C(5)−F(6)	1.30(3)
C(1)−C(2)	1.49(3)	C(5)−C(4)	1.42(3)
(d) Angles around Gallium			
O(1)−Ga(1)−O(5)	88.7(4)	O(5)−Ga(1)−C(11)	104.0(5)
O(1)−Ga(1)−C(11)	111.4(5)	O(5)−Ga(1)−C(21)	109.1(5)
O(1)−Ga(1)−C(21)	103.8(6)	C(11)−Ga(1)−C(21)	131.5(8)

vantage as the metathesis reaction. The reagent $Ga(bdk)_3$ must be independently prepared before the synthesis of $R_2Ga(bdk)$ can be attempted. When the ligand redistribution reaction was used, the choice of solvent was important to the success of the reaction. The yield of $Mes_2Ga(hfac)$ was about 85% when Et_2O was used. In contrast, when the solvent was benzene, only a 25% yield of product was isolated under the identical reaction conditions of time and temperature.

An X-ray structural study of $Mes_2Ga(hfac)$ confirmed the bidentate nature of the β-diketonate ligand bonded to the gallium center. The molecular geometry and labeling of atoms is shown in Figure 1. Interatomic distances and angles are collected in Table 1. The central gallium atom is in a very distorted tetrahedral environment. The hexafluoroacetyl-acetonate moiety behaves as a typical chelating ligand and is linked to gallium by two equivalent bonds (Ga(1)−O(1) = 2.008(11) Å and Ga(1)−O(5) = 2.009(11) Å) with a bite angle of O(1)−Ga(1)−O(5) = 88.7(4)°. These Ga−O bond lengths are slightly longer than those found for $Ga(hfac)_3$,[6] which range from 1.942(5) to 1.971(5) Å (average 1.954(5) Å). The two bulky mesityl ligands are separated by the expanded angle of C(11)−Ga(1)−C(21) = 131.5(8)° and are associated with the gallium−carbon bond lengths Ga(1)−C(11) = 1.971(13) Å and Ga(1)−C(21) = 1.943(10) Å (average 1.957 Å), a distance comparable to that in $GaMes_3$ (1.968(4) Å).[7] Distances within the metallacyclic ring are symmetrical, with O(1)−C(2) = 1.245(20) Å versus O(5)−C(4) = 1.252(21) Å and C(2)−C(3) = 1.392(24) Å versus C(3)−C(4) = 1.422(23) Å. The $C-CF_3$ bonds have values consistent with their $C(sp^2)-C(sp^3)$ nature (C(1)−C(2) = 1.49(3) Å and C(4)−C(5) = 1.42(3) Å). The structure is marred by extremely large "thermal vibration ellipsoids" for the fluorine atoms. These large ellipsoids are consistent with large librational motion or hindered rotation of the CF_3 groups about their $C-CF_3$ bonds and give rise to some artificially contracted C−F bond lengths (C−F = 1.18(3) − 1.30(3) Å as compared to the normal $C(sp^3)-F$ distance of 1.333 ± 0.005 Å in polyfluorinated systems[8]). Similar effects have been observed previously for molecules such as $(\eta^5\text{-}C_5H_5)Rh[\eta^4\text{-}C_6(CF_3)_6]$.[9−11]

The physical and spectroscopic properties of all 12 diorganogallium β-diketonate compounds are consistent with the presence of the bidentate ligand and four-coordinate gallium. Cryoscopic molecular weight studies demonstrate the compounds to be monomeric in benzene solution. The compounds are typically liquids and can be distilled or sublimed quantitatively under reduced pressure (10^{-4} mmHg) without decomposition at about room temperature. The volatility was observed to increase as the extent of fluorine sustitution on the β-diketonate ligand increased. This same trend has been observed for $M(bdk)_3$ (M = Al, Ga, In)[12] and for other metallic systems.[13] None of the current compounds are pyrophoric. The C=O stretching vibrations[14] for $R_2Ga(bdk)$ were observed in the range of 1643−1648 cm^{-1} for hfac compounds, 1575−1590 cm^{-1} for the acac compounds, and 1597−1599 cm^{-1} for tmhd compounds. These bands are at significantly lower energies than those found for the free ligands (1689 cm^{-1}, H(hfac); 1728 cm^{-1}, H(acac); 1720 cm^{-1}, H(tmhd)) and are indicative of β-diketonate chelation to the metal center. It should be noted, however, that such lowering of the stretching frequencies for the metal derivatives relative to the free ligand is not conclusive evidence for carbonyl coordination to the metal center, as the C=O stretching frequency for $Me_2Ga(tfac)$ was assigned to the very strong and relatively sharp band at 1620 cm^{-1}, whereas the free ligand had a very strong and broad band centered around 1600 cm^{-1}. The apparent differ-

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ence in C=O stretching frequencies between Me_2Ga(tfac) and other diorganogallium β-diketonates may be attributed to the mixing of modes due to the asymmetrical nature of the β-diketonate ligand. The room-temperature ^1H, ^{13}C, and ^{19}F NMR spectra of benzene solutions of the diorganogallium β-diketonates are typical of compounds with chelated structures.

The potential of the diorganogallium β-diketonates which were prepared in this study to react with the Lewis base NMe_3 was examined by tensimetric titrations. The goals were to determine whether these four-coordinate gallium compounds would exhibit Lewis acidity and, if they were Lewis acids, to identify the site of acidity and to elucidate the factors which appear to control the relative Lewis acidities of the diorganogallium β-diketonate derivatives. Lewis acidity was observed and was found to be dependent upon the β-diketonate and the organic ligands bound to the gallium center. Only the fluorinated derivatives Me_2Ga(hfac) and Me_2Ga(tfac) in the series Me_2Ga(bdk) (bdk = hfac, tfac, acac, tmhd) reacted with NMe_3 to form 1:1 Lewis adducts, and only $Me_2Ga(hfac)\cdot NMe_3$ was stable to dissociation at room temperature. Furthermore, in the series R_2Ga(hfac) (R = Me, Et, Mes) only the methyl and ethyl derivatives formed 1:1 Lewis adducts according to the tensimetric titration data but $Et_2Ga(hfac)\cdot NMe_3$ was unstable with respect to dissociation of NMe_3 at room temperature. The two adducts which were isolated at room temperature, $Me_2Ga(hfac)\cdot py$ and $Me_2Ga(hfac)\cdot NMe_3$, decompose at approximately 100 °C, as indicated by the change in slope in their plots of vapor pressure versus temperature and by the appearance of an orange-brown liquid with a brown solid on the sides of the tensimeter. Furthermore, thermal analysis of $Me_2Ga(hfac)\cdot py$ by using a DSC operating at a heating rate of 10 °C/min exhibited a sharp endotherm at 43.5 °C (mp 45.7−47.5 °C) and a broad endotherm with a peak at 102.3 °C, an endotherm consistent with decomposition. The nature of the decomposition was not studied.

There are two possible sites for the coordination of a Lewis base to a diorganogallium β-diketonate, either the gallium atom or the carbonyl carbon of the ligand. Since $Me_2Ga(hfac)\cdot NMe_3$ was not conducive to an X-ray structural study in our laboratory because of its low melting point (29.9−31.3 °C), the site of coordination of an amine to Me_2Ga(hfac) in the solid state was elucidated by an X-ray structural study of $Me_2Ga(hfac)\cdot py$ (mp 45.7−47.5 °C). The pyridine is bonded to the gallium center. The molecular structure and labeling of the atoms are shown in Figure 2. Interatomic distances and angles are collected in Table 2. The central gallium atom has an unusual sterochemistry, as it is essentially a distorted trigonal bipyramid with one very long (and presumably very weak) bond to oxygen and four more normal bonds: one to oxygen, one to nitrogen, and two to carbon atoms. Thus, the hexafluoroacetylacetonate ligand is associated with very asymmetric bonds to gallium with a Ga(1)−O(1) distance of 1.971(8) Å and another very long distance of 2.590(8) Å for Ga(1)···O(2). The compound with five-coordinate gallium atoms[15] $\{Me_2Ga[OCH(Me)_2CH_2NMe_2]\}_2$ has Ga−O distances of 1.919(2) Å (equatorial) and 2.097(2) Å (axial). The Ga−O bond lengths in oxygen adducts of triorganogallium compounds are 2.047 Å (average) for $(Mes)_3Ga\cdot OH_2\cdot 2THF$,[16] 2.107(6) Å for $(o\text{-}MeC_6H_4)_3Ga\cdot OEt_2$,[17] and 2.069(7) Å for $(C_6H_5CH_2)_3Ga\cdot THF$.[18] In contrast, the gallium−oxygen distance for the six-coordinate gallium compound $Ga(hfac)_3$[6] is 1.954(5) Å, whereas for Mes_2Ga(hfac) it is 2.009(11) Å. It may also be noted that the shorter Ga(1)−O(1) bond length in $Me_2Ga(hfac)\cdot py$ is slightly longer than the Ga−O average bond lengths found for $[(C_5H_5)_2GaOEt]_2$[19] (1.906(3) Å), $[Me_2GaOH]_4$[20] (1.96 Å), $[^tBu_2GaOH]_3$,[21] (1.957(5) Å), and $[Mes_2GaOH]_2\cdot THF$[16] (1.949(2) Å). The remaining gallium-to-ligand bonds are normal and internally consistent, viz., Ga(1)−N(1) = 2.128(9) Å and the $Ga-CH_3$ linkages Ga(1)−C(21) = 1.986(13) Å and Ga(1)−C(22) = 1.941(14) Å (average $Ga-CH_3$ = 1.964 Å). This Ga−N distance is comparable to that found for $Ga(N_3)_3\cdot 3py$,[22] where the average Ga−N(py) distance is 2.131(4) Å. Bond lengths around the six-membered Ga−O−C−C−C−O system are consistent with some bond alternation, with Ga(1)−O(1) = 1.971(8) Å (short), O(1)−C(2) = 1.287(15) Å (long), C(2)−C(3) = 1.346(16) Å (short), C(3)−C(4) = 1.386(16) Å (long), C(4)−O(2) = 1.251(17) Å (short), and O(2)···Ga(1) =

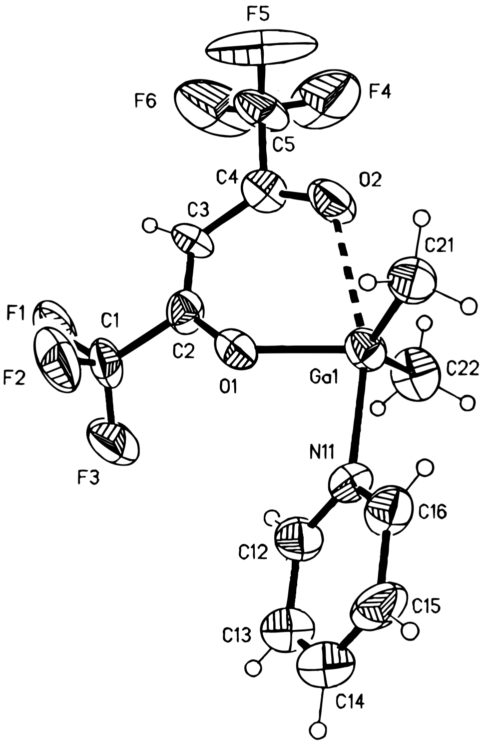

Figure 2. Molecular geometry of $Me_2Ga(hfac)\cdot NC_5H_5$ (ORTEP2 diagram, 30% probability envelopes for thermal vibration ellipsoids, with hydrogen atoms artificially reduced).

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Me$_2$Ga(hfac)·NC$_5$H$_5$

(a) Gallium−Ligand Distances			
Ga(1)−O(1)	1.971(8)	Ga(1)−C(21)	1.986(13)
Ga(1)···O(2)	2.590(8)	Ga(1)−C(22)	1.941(14)
Ga(1)−N(11)	2.128(9)		
(b) Bond Lengths within “Chelate” Ring			
O(1)−C(2)	1.287(15)	C(2)−C(3)	1.346(16)
O(2)−C(4)	1.251(17)	C(3)−C(4)	1.386(16)
(c) Bond Lengths Involving CF$_3$ Groups			
C(1)−F(1)	1.311(18)	C(5)−F(4)	1.302(24)
C(1)−F(2)	1.315(17)	C(5)−F(5)	1.172(25)
C(1)−F(3)	1.288(17)	C(5)−F(6)	1.177(27)
C(1)−C(2)	1.486(18)	C(5)−C(4)	1.507(21)
(d) Bond Lengths within Pyridine Ring			
N(11)−C(12)	1.335(17)	C(13)−C(14)	1.313(29)
N(11)−C(16)	1.297(16)	C(14)−C(15)	1.380(26)
C(12)−C(13)	1.430(21)	C(15)−C(16)	1.369(19)
(e) Angles around Gallium			
O(1)−Ga(1)−N(11)	85.8(3)	O(1)−Ga(1)−C(21)	112.2(5)
O(1)−Ga(1)−C(11)	111.4(5)	O(5)−Ga(1)−C(21)	109.1(5)
N(11)−Ga(1)−C(21)	101.8(4)	O(1)−Ga(1)−C(22)	109.9(5)
N(11)−Ga(1)−C(22)	101.0(5)	C(21)−Ga(1)−C(22)	133.0(6)
O(2)···Ga(1)−O(1)	76.5(3)	O(2)···Ga(1)−N(11)	162.3(3)
O(2)···Ga(1)−C(21)	84.8(5)	O(2)···Ga(1)−C(22)	85.8(5)
(f) Angles within the CF$_3$COCHCOCF$_3$ Ligand			
Ga(1)−O(1)−C(2)	134.6(7)	Ga(1)···O(2)−C(4)	120.7(8)
C(2)−C(1)−F(1)	112.6(11)	C(2)−C(1)−F(2)	111.0(11)
F(1)−C(1)−F(2)	103.5(12)	C(2)−C(1)−F(3)	115.9(12)
F(1)−C(1)−F(3)	108.4(12)	F(2)−C(1)−F(3)	104.5(11)
O(1)−C(2)−C(1)	109.2(10)	O(1)−C(2)−C(3)	130.4(11)
C(1)−C(2)−C(3)	120.3(11)	C(2)−C(3)−C(4)	123.3(11)
O(2)−C(4)−C(3)	127.2(11)	O(2)−C(4)−C(5)	115.3(12)
C(3)−C(4)−C(5)	117.2(13)	C(4)−C(5)−F(4)	109.0(18)
C(4)−C(5)−F(5)	116.0(16)	F(4)−C(5)−F(5)	99.1(16)
C(4)−C(5)−F(6)	117.1(14)	F(4)−C(5)−F(6)	97.8(17)
(g) Angles Involving the Pyridine Moiety			
Ga(1)−N(11)−C(12)	120.4(8)	Ga(1)−N(11)−C(16)	124.3(8)
C(12)−N(11)−C(16)	115.4(11)	N(11)−C(12)−C(13)	121.8(14)
C(12)−C(13)−C(14)	120.1(17)	C(13)−C(14)−C(15)	118.1(16)
C(14)−C(15)−C(16)	118.2(16)	N(11)−C(16)−C(15)	126.3(13)

2.590(8) Å (long); unfortunately, differences between C−O and C−C bonds are on the borderline of statistical significance. Using the trigonal bipyramid description for the coordination about Ga(1), the diaxial angle is then O(2)···Ga(1)−N(11) = 162.3(3)° and the diequatorial angles are O(1)−Ga(1)−C(21) = 112.2(5)°, O(1)−Ga(1)−C(22) = 109.9(5)°, and C(21)−Ga(1)−C(22) = 133.0(6)°. The CF$_3$ centered on C(1) is well-behaved with C(1)−F = 1.288(17)−1.315(17) Å, whereas that centered on C(5) shows once again the effects of libration and has some artifically reduced carbon−fluorine distances (C(5)−F = 1.172(25), 1.177(27), and 1.302(24) Å).

The properties of the trimethylamine and pyridine adducts of Me$_2$Ga(hfac) in benzene solution were also investigated in order to learn more the nature of gallium-base interaction. The compound Me$_2$Ga(hfac)·NMe$_3$ was monomeric and was not dissociated in benzene solution according to cryoscopic molecular weight studies. There was no dependence of the observed molecular weight on the concentration of the solution. On the other hand, Me$_2$Ga(hfac)·py was partially dissociated in solution. The observed molecular weight was concentration-dependent. As the solution was diluted, the observed molecular weight decreased. Thus, pyridine would appear to be a weaker Lewis base than is trimethylamine in benzene solution.

The infrared and NMR spectra of Me$_2$Ga(hfac)·NMe$_3$ and Me$_2$Ga(hfac)·py are consistent with the hypothesis that the Lewis base is bonded to gallium rather than to a carbonyl carbon atom. If the observed bands at 1685 and 1683 cm^{-1} for Me$_2$Ga(hfac)·NMe$_3$ and Me$_2$Ga(hfac)·py, respectively, are assigned to the carbonyl stretching frequencies,[14] the adducts have stronger carbon−oxygen bonds and weaker metal−carbonyl interactions than does Me$_2$Ga(hfac). The corresponding band for the parent compound Me$_2$Ga(hfac) occurs at 1645 cm^{-1}, whereas it is 1689 cm^{-1} for the free ligand H(hfac). The NMR spectra of benzene solutions of the two adducts suggest that the β-diketonate ligand and the amine undergo very rapid exchange processes in solution, even at −70 °C, the lowest temperature studied. The ^{13}C NMR spectrum at the normal operating temperature of the instrument indicated only one type of carbonyl carbon atom and one type of trifluoromethyl carbon atom for each adduct, whereas the corresponding ^{19}F NMR spectra had only one apparent signal for the trifluoromethyl groups of each compound. Similarily, the room-temperature ^{1}H NMR spectra of benzene solutions of these compounds had one set of signals for each compound, one for the unique hfac-H proton, one for the CH$_3$ group bonded to gallium, and only one signal or set of signals attributable to the appropriate amine. The line for the gallium methyl protons for a specific adduct is at lower field than for Me$_2$Ga(hfac), whereas the line for the base protons is at higher field than for the free base. The reverse situation is observed for typical adducts.[23] The gallium methyl lines of the adduct are typically at higher field than for the free acid, and amine protons for the adduct are at lower field than for the free Lewis base. Variable-temperature ^{1}H NMR spectra of toluene solutions of Me$_2$Ga(hfac)·py and Me$_2$Ga(hfac)·NMe$_3$ over a temperature range of −70 to +110 °C were also recorded. The spectra did not change in appearance when compared with those observed at the normal operating temperature of the instrument. However, with increasing temperature, the amine resonances moved downfield toward the chemical shift observed for the free amine while the resonances for the unique hfac proton and the Ga−CH$_3$ protons moved upfield toward the chemical shifts observed for a benzene solution of Me$_2$Ga(hfac). These observations suggest that the gallium−nitrogen bonds of the adducts are more dissociated at the higher temperatures, as expected.

Attempts to prepare MeGa(bdk)$_2$ (bdk = hfac, acac) and MesGa(hfac)$_2$ by elimination and ligand redistribution reactions were unsuccessful. The products were mixtures of R$_2$Ga(bdk) and Ga(bdk)$_3$. Thus, these observations are consistent with the chemistry observed for the corresponding organoaluminum β-diketonate compounds[2] and might reflect the preferential coordination numbers of 4 and 6 rather than 5 for gallium and aluminum.

Experimental Section

All compounds described in this investigation were manipulated in a standard vacuum line or under a purified argon atmosphere. The starting materials GaMe$_3$ and GaEt$_3$ were

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(23) Beachley, O. T., Jr.; Maloney, J. D. *Organometallics* **1997**, *16*, 4016.

purchased from Strem Chemical and vacuum distilled prior to use. Trimesitylgallium(III) was prepared and purified according to literature procedure.[7] The starting material $GaCl_3$ was purchased from Strem Chemical and sublimed under dynamic vacuum prior to each use. The β-diketones were purchased from Aldrich Chemical Co., dried over K_2CO_3, and vacuum-distilled prior to use. The sodium β-diketonates were prepared according to literature procedures.[24] Dimethylgallium chloride[25] and diethylgallium chloride[26] were prepared by stoichiometric ligand redistribution reactions in pentane at room temperature and were purified by vacuum sublimation at room temperature and by vacuum distillation at 37 °C, respectively. The compound $Ga(acac)_3$ was purchased from Strem Chemicals and was used without further purification. Tris(hexafluoroacetylacetonato)gallium(III) was prepared by a metathesis reaction between $GaCl_3$ and Na(hfac) in a 1:3 mol ratio in pentane and was purified by room-temperature sublimation under dynamic vacuum (10^{-4} mmHg). The melting point and IR spectrum were in agreement with published data.[6] Pyridine and NMe_3 were dried over KOH and distilled prior to use. All solvents were dried by conventional procedures. Infrared spectra of the compounds either as liquids or as Nujol mulls of solids between CsI plates were recorded by using a Perkin-Elmer Model 683 spectrometer. Absorption intensities are reported with the abbreviations w (weak), m (medium), s (strong), vs (very strong), and sh (shoulder). Elemental analyses were performed by E+R Microanalytical Laboratories, Inc., Corona, NY. The ^1H NMR (400 MHz) and ^{19}F NMR (376.3 MHz) spectra were recorded by using a Varian Unity-Inova 400 spectrometer. The ^{13}C NMR (75 MHz) spectra were recorded on a Varian Gemini 300 spectrometer. The ^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were obtained by a Varian Unity-Inova 500 spectrometer. Proton chemical shifts are reported in δ (ppm) units and are referenced to C_6D_5H at 7.15 ppm and $SiMe_4$ at 0.00 ppm. Carbon chemical shifts are referenced to $SiMe_4$ at 0.00 ppm and ^{13}C impurities in C_6D_6 at 128.39 ppm. Fluorine chemical shifts were referenced to $CF_3C_6H_5$ at 0.00 ppm. The following abbreviations are used to report the multiplicities of lines: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). All samples for NMR spectroscopic studies were contained in sealed tubes. Melting points were observed for samples which were contained in sealed capillaries filled with purified argon and are uncorrected. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdon.[27a]

Synthesis of $R_2Ga(bdk)$ by Elimination Reactions (Method A). The preparation of all diorganogallium β-diketonate compounds by elimination reactions was accomplished by combining stoichiometric quantities of GaR_3 and the β-diketone in pentane, essentially the same method reported by Coates and Hayter[4] except that solvent was used. In a typical preparation, 0.823 g (7.23 mmol) of $GaMe_3$ and 30 mL of pentane were vacuum-distilled into a 250 mL round-bottomed flask fitted with a stir bar and connected to a 100 mL Schlenk flask by a glass elbow. Then, 1.50 g (7.23 mmol) of hfacH was added by vacuum distillation at −196 °C. As the reaction mixture was slowly warmed to room temperature with stirring, vigorous methane evolution occurred for about 10 min. The resulting yellow solution was stirred at room temperature for 12 h to ensure complete reaction. The methane and pentane were separated from the product by vacuum distillation by holding the reaction flask at −20 °C (alcohol/ice). Then, the product was isolated and purified by repeated fractional dynamic vacuum distillations by using −20 and −196 °C traps. The yellow crystalline solid which remained in the −20 °C trap was further purified by vacuum distillation at room temperature to yield $Me_2Ga(hfac)$ (2.22 g, 7.23 mmol, 91.6% yield based on Hhfac).

Synthesis of $R_2Ga(hfac)$ ($R = Me, Et$) by Metathesis Reactions (Method B). The preparation of $R_2Ga(hfac)$ ($R =$ Me, Et) by metathesis reactions was accomplished by combining stoichiometric quantities of GaR_2Cl and Na(hfac) in pentane. In a typical experiment a Solv-Seal two-necked flask was charged with the appropriate diorganogallium chloride (3−7 mmol), was equipped with a magnetic stir bar and a sidearm dumper containing a stoichiometric quantity of Na(hfac), and was connected to another Solv-Seal Schlenk flask with a medium-porosity glass frit. Next, approximately 30 mL of pentane was vacuum-distilled onto the diorganogallium chloride at −196 °C. With the solution of R_2GaCl at 0 °C, Na(hfac) was added over a period of 20 min. After the reaction mixture had been stirred at room temperature for 12 h, the resulting yellow product was filtered. The diorganogallium β-diketonate was separated from the solvent by fractional distillations by using −20 and −196 °C baths as described previously.

Synthesis of $R_2Ga(bdk)$ ($R = Me$, bdk = hfac, acac; $R=$ Mes, bdk = hfac) by Ligand Redistribution Reactions (Method C). In a typical reaction, the reagents GaR_3 and $Ga(bdk)_3$ were added to a reaction flask equipped with a magnetic stir bar. Then, approximately 25 mL of solvent (pentane for $Me_2Ga(hfac)$; Et_2O for $Me_2Ga(acac)$) was vacuum-distilled into the flask. The reaction mixture was warmed to room temperature, stirred, and subsequently heated in a 70 °C oil bath for 2 h. Then, the resulting clear solution was stirred overnight at room temperature. In the case of $Mes_2Ga(hfac)$, an additional heating period of 3 h was required for complete reaction. The solvent was removed while the reaction mixture was held at −20 °C. Purification of the product was achieved by either fractional vacuum distillation or vacuum sublimation, as appropriate.

Tensimetric Titrations. The diorganogallium β-diketonate derivatives which reacted with NMe_3 were determined by tensiometric titrations at 0 °C either as the neat species or as toluene solutions ($Mes_2Ga(bdk)$, bdk = hfac, acac, tmhd) as described by Shriver and Drezdon.[27b] Those diorganogallium β-diketonate derivatives which formed stoichiometric adducts were subsequently prepared, isolated, and characterized.

Preparation of Lewis Adducts. A preweighed amount (1−10 mmol) of $R_2Ga(hfac)$ ($R =$ Me, Et) was vacuum-distilled into a flask at −196 °C which was connected by a glass elbow to another Schlenk flask. After an excess of amine was added by vacuum distillation, the reaction mixture was stirred for 1 h at room temperature. The excess amine was removed at 0 °C by vacuum distillation. The resulting product was then purified at room temperature by either vacuum sublimation ($Me_2Ga(hfac)\cdot NMe_3$, $Me_2Ga(hfac)\cdot py$) or vacuum distillation ($Et_2Ga(hfac)\cdot NMe_3$).

Determination of Vapor Pressure as a Function of Temperature. The vapor pressure of each diorganogallium β-diketonate derivative was observed at room temperature and above by using an immersible tensimeter that was connected to the manometer on the vacuum line.[27c] Mercury heights were measured by using a cathetometer which could be read to ±0.01 mmHg.

Synthetic Reaction and Product Characterization Data. $Me_2Ga(hfac)$. Yield of product: method A, 91.6%; method B, 73.6%; method C, 78.8%. Mp: yellow liquid at room temperature; liquid easily supercooled; crystals formed by maintaining pure compound at 0 °C for 2 h. Vp at 20 °C: 13.9 mmHg ($\log p = -2155/T + 8.45$, $R^2 = 0.999$). Cryoscopic molecular weight, benzene solution, formula weight 306.84 (observed molality, observed mol wt, association): 0.0605, 274, 0.89; 0.0490, 261, 0.85; 0.0318, 266, 0.87. Anal. Calcd for

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$\mathrm{C_7H_7F_6GaO_2}$: C, 27.40; H, 2.30. Found: C, 27.65; H, 2.43. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 5.80 (s, 0.7 H, *H*-hfac), −0.26 ($\mathrm{Ga{-}C}H_3$, 6H). ^{13}C NMR (75.46 MHz, $\mathrm{C_6D_6}$): δ 181.08 (q, $J_{\mathrm{CO-F}} = 37.7$ Hz, −C=O), 117.84 (q, $J_{\mathrm{C-F}} = 287$ Hz, $-\mathrm{CF_3}$), 91.31 (s, =C−), −6.17 (s, $\mathrm{H_3C{-}Ga}$). ^{19}F NMR ($\mathrm{C_6D_6}$): δ −14.38. IR (neat, cm^{-1}): 1735 (w), 1700 (w), 1652 (sh, s), 1645 (vs), 1615 (sh, m), 1611 (m), 1562 (m), 1534 (m), 1500 (w), 1451 (vs), 1355 (w), 1332 (w), 1255 (vs). Vapor pressure vs temperature data (1/*T* (×10^{-3}) [log p]): 3.382 [1.161], 3.272 [1.446], 3.163 [1.678], 2.984 [2.045], 2.872 [2.291], 2.800 [2.439], 2.713 [2.622], 2.644 [2.78].

$\mathbf{Me_2Ga(hfac)\cdot NMe_3}$. Colorless crystalline solid. Mp: 29.9−31.3 °C. Vp at 20 °C: 2.0 mmHg ($\log p = -2281/T + 8.44$, $R^2 = 0.978$). Cryoscopic molecular weight, benzene solution, formula weight 365.95 (observed molality, observed mol wt, association): 0.0631, 348, 0.95; 0.0496, 343, 0.94; 0.0323, 344, 0.94. Anal. Calcd for $\mathrm{C_{10}H_{16}F_6GaNO_2}$: C, 32.82; H, 4.41; N, 3.83. Found: C, 32.80; H, 4.52; N, 3.72. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ 6.08 (s, 0.6 H, *H*-hfac), 1.62 (s, 9 H, $\mathrm{NC}H_3$), −0.16 (s, 6 H, $\mathrm{Ga{-}C}H_3$). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$): δ 175.97 (q, $^2J_{\mathrm{CF}} =$ 34 Hz, C=O), 118.77 (q, $J_{\mathrm{CF}} = 288$ Hz, $-\mathrm{CF_3}$), 90.41 (s, =C−), 46.46 (s, $\mathrm{N{-}CH_3}$), −7.073 (s, $\mathrm{Ga{-}CH_3}$). ^{19}F NMR ($\mathrm{C_6D_6}$): δ −14.39. IR (Nujol mull, cm^{-1}): 1685 (s), 1646 (m), 1605 (w), 1557 (s), 1529 (m), 1480 (s), 1447 (m), 1408 (w). Vapor pressure vs temperature data (1/*T* (×10^{-3}) [log *p*]): 3.66 [0.155], 3.31 [0.708], 3.27 [0.892], 3.1 [1.358], 3 [1.627], 2.92 [1.832], 2.83 [2.062], 2.74 [2.306], 2.7 [2.413], 2.61 [2.577], 2.54 [2.605], 2.45 [2.588].

$\mathbf{Me_2Ga(hfac)\cdot py}$. Lilac colored solid before complete removal of excess pyridine and colorless crystalline solid after purification by room-temperature vacuum sublimation; isolated in 85.6% yield. Mp: 45.7−47.5 °C. Vp at 20 °C: 0.4 mmHg ($\log \mathrm{p} = -2404/T + 8.41$, $R^2 = 0.976$). Cryoscopic molecular weight, benzene solution, formula weight 385.94 (observed molality, observed mol wt, association): 0.08342, 345, 0.89; 0.0703, 336, 0.87; 0.0528, 295, 0.76. Anal. Calcd for $\mathrm{C_{12}H_{12}F_6GaNO_2}$: C, 37.35; H, 3.13; N, 3.63. Found: C, 37.53; H, 3.07; N, 3.63. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ 8.13 (m, py), 6.75 (m, py), 6.42 (m, py), 6.13 (s, 0.7 H, *H*-hfac), 0.09 (s, 6 H, $\mathrm{Ga{-}C}H_3$). ^{13}C NMR (125.7 MHz, $\mathrm{C_6D_6}$): δ 176.99 (q, $^2J_{\mathrm{CF}} = 35$ Hz, C=O), 147.53 (s, py), 138.60 (s, py), 125.00 (s, py), 118.53 (q, $J_{\mathrm{CF}} = 286$ Hz, $-\mathrm{CF_3}$), 90.81 (s, =C−), −4.14 (s, $\mathrm{Ga{-}CH_3}$). ^{19}F NMR ($\mathrm{C_6D_6}$): δ −14.31. IR (Nujol mull, cm^{-1}): 1740 (m, sh), 1683 (vs), 1656 (s, sh), 1610 (s), 1557 (s), 1533 (s), 1472 (vs, br), 1397 (m). Vapor pressure vs temperature data (1/*T* (×10^{-3}) [log p]): 3.4 [0.176], 3.37 [0.204], 3.27 [0.398], 3.19 [0.653], 3.13 [0.833], 3.08 [0.987], 3.02 [1.215], 2.97 [1.348], 2.87 [1.632], 2.86 [1.688], 2.8 [1.803], 2.75 [1.897], 2.68 [2.131], 2.61 [2.26], 2.51 [2.404], 2.5 [2.408], 2.44 [2.448], 2.41 [2.457], 2.34 [2.485].

$\mathbf{Et_2Ga(hfac)}$. Yield of product: method A, 94.9%; method B, 85.5%. Brilliant yellow liquid purified by room-temperature vacuum distillation. Vp at 20 °C: 2.2 mmHg. Cryoscopic molecular weight, benzene solution, formula weight 334.90 (observed molality, observed mol wt, association): 0.0826, 330, 0.98; 0.0615, 328, 0.98; 0.0412, 326, 0.97. Anal. Calcd for $\mathrm{C_9H_{11}F_6GaO_2}$: C, 32.28; H, 3.31. Found: C, 32.30; H, 3.24. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ 5.86 (*H*-hfac, 0.7 H), 0.95 (t, $J_{\mathrm{CH}} = 8$ Hz, $\mathrm{GaCH_2C}H_3$), 0.42 (q, $J_{\mathrm{CH}} = 8$ Hz, $\mathrm{Ga{-}C}H_2$). ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$): δ 181.53 (q, $J_{\mathrm{COF}} = 36$ Hz, −C=O), 117.90 (q, $J_{\mathrm{CF}} = 285$ Hz, $-\mathrm{CF_3}$), 91.38 (s, =C−), 8.31 (s, $\mathrm{GaCH_2CH_3}$), 5.55 (s, $\mathrm{GaCH_2CH_3}$). ^{19}F NMR ($\mathrm{C_6D_6}$): δ −14.36. IR (neat, cm^{-1}): 1765 (w), 1648 (vs), 1615 (m), 1565 (m), 1538 (w), 1453 (s).

$\mathbf{Et_2Ga(hfac)\cdot NMe_3}$. Brilliant yellow liquid isolated in 73.7% yield by vacuum distillation at room temperature. Vp at 20 °C: 1.5 mmHg. Cryoscopic molecular weight, benzene solution, formula weight 394.01 (observed molality, observed mol wt, association): 0.0822, 349, 0.89; 0.0670, 346, 0.88; 0.0466, 344, 0.87. Anal. Calcd for $\mathrm{C_{12}H_{20}F_6GaNO_2}$: C, 36.58; H, 5.12. Found: C, 36.60; H, 4.64. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ 6.04 (s, 0.7 H, *H*-hfac), 1.68 (s, 9 H, $\mathrm{NC}H_3$), 1.14 (t, $J_{\mathrm{CH}} = 8$ Hz, 6 H, $\mathrm{GaCH_2C}H_3$), 0.45 (t, $J_{\mathrm{CH}} = 8$ Hz, 4 H, $\mathrm{GaC}H_2\mathrm{CH_3}$). ^{13}C NMR (125.7 MHz, $\mathrm{C_6D_6}$): δ 203.29 (q, $^2J_{\mathrm{CF}} = 36$ Hz, C=O), 46.80 (s, $\mathrm{NCH_3}$), 9.84 (s, $\mathrm{GaCH_2CH_3}$), 5.43 (s, $\mathrm{GaCH_2CH_3}$). IR (neat, cm^{-1}): 1648 (s), 1613 (w), 1580 (w), 1565 (w), 1539 (w), 1477 (w), 1455 (m).

$\mathbf{Mes_2Ga(hfac)}$. Yield of product: method A, 65.7%; method C, 87.3%. Bright yellow solid purified by recrystallization from methylcyclohexane at −20 °C (crystallographic quality crystals) or by vacuum sublimation at 60 °C. Mp: 91.1−93.4 °C. Cryoscopic molecular weight, benzene solution, formula weight 515.14 (observed molality, observed mol wt, association): 0.0620, 601, 1.17; 0.0540, 570, 1.11; 0.0367, 561, 1.09. Anal. Calcd for $\mathrm{C_{23}H_{23}F_6GaO_2}$: C, 53.63; H, 4.50. Found: C, 53.81; H, 4.51. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ 6.73 (s, 2H, Mes-H), 5.83 (s, 0.7 H, *H*-hfac), 2.38 (s, 12H, *o*-Mes-C*H*$_3$), 2.10 (s, 6H, *p*-Mes-C*H*$_3$). ^{13}C NMR (125.7 MHz, $\mathrm{C_6D_6}$): δ 180.48 (q, $^2J_{\mathrm{CF}} = 36$ Hz, C=O), 144.93 (s, Mes), 140.00 (s, Mes), 138.86 (s, Mes), 128.89 (s, Mes), 117.70 (q, $J_{\mathrm{CF}} = 284$ Hz, $-\mathrm{CF_3}$), 92.33 (s, =C−), 24.64 (s, *o*-Mes-$\mathrm{CH_3}$), 21.49 (s, *p*-Mes-$\mathrm{CH_3}$). ^{19}F NMR ($\mathrm{C_6D_6}$): δ −14.36. IR (Nujol mull, cm^{-1}): 1643 (m), 1609 (w), 1602 (w), 1562 (m), 1535 (w), 1458 (s), 1446 (sh, s), 1436 (sh, m), 1365 (sh, m), 1356 (sh, w), 1340 (sh, w), 1287 (w).

$\mathbf{Me_2Ga(tfac)}$. Yield of product: method A, 93.4%. Colorless liquid. Vp at 20 °C: 3.1 mmHg ($\log p = -2172/T + 7.99$, $R^2 = 0.997$). Cryoscopic molecular weight, benzene solution, formula weight 252.87 (observed molality, observed mol wt, association): 0.0794, 238, 0.94; 0.0644, 234, 0.93; 0.0438, 232, 0.92. Anal. Calcd for $\mathrm{C_7H_{10}F_3GaO_2}$: C, 33.25; H, 3.99. Found: C, 33.20; H, 3.90. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ 5.35 (s, 0.5 H, *H*-hfac), 1.34 (s, 3 H, tfac-C*H*$_3$), 0.42 (s, 6 H, $\mathrm{Ga{-}C}H_3$). ^{13}C NMR (125.7 MHz, $\mathrm{C_6D_6}$): δ 202.90 (s, $\mathrm{H_3CC{=}O}$), 171.66 (q, $^2J_{\mathrm{CF}} = 34$ Hz, −C=O), 121.49 (q, $J_{\mathrm{CF}} = 283$ Hz, $-\mathrm{CF_3}$), 96.59 (s, =C−), 28.46 (s, tfac-$\mathrm{CH_3}$), −6.14 (s, $\mathrm{GaCH_3}$). IR (neat, cm^{-1}): 1729 (w), 1620 (vs), 1527 (vs), 1442 (vs), 1365 (vs), 1300 (br, vs). Vapor pressure vs temperature data (1/*T* (×10^{-3}) [log *p*): 2.493 [2.603], 2.596 [2.377], 2.623 [2.215], 2.821 [1.895], 2.918 [1.667], 3.006 [1.459], 3.082 [1.26], 3.229 [0.973], 3.31 [0.82].

$\mathbf{Me_2Ga(acac)}$. Yield of product: method A, 96.3%; method C, 78.0%. Colorless solid. Mp: 20−22 °C (lit.[4] mp 21.8−22.0 °C). Vp at 20 °C: 1.1 mmHg (lit[4] mp 1.1 mmHg). Cryoscopic molecular weight, benzene solution, formula weight 198.90 (observed molality, observed mol wt, association): 0.100, 186, 0.93; 0.0786, 179, 0.90; 0.0561, 174.46, 0.88. Anal. Calcd for $\mathrm{C_7H_{13}GaO_2}$: C, 42.27; H, 6.59. Found: C, 42.49; H, 6.39. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ 4.92 (*H*-acac, 0.7 H), 1.58 (s, 6 H, acac-C*H*$_3$), 0.03 (s, 6 H, $\mathrm{Ga{-}C}H_3$). ^{13}C NMR (125.7 MHz, $\mathrm{C_6D_6}$): δ 193.33 (s, −C=O), 100.71 (s, =C−), 27.41 (s, acac−$\mathrm{CH_3}$), −6.22 (s, $\mathrm{Ga{-}CH_3}$). IR (neat, cm^{-1}): 1590 (vs), 1530 (s), 1430 (s), 1370 (vs).

$\mathbf{Et_2Ga(acac)}$. Yield of product: method A, 89.2%. Colorless liquid purified by vacuum distillation at 27 °C by using a short-path distillation apparatus. Cryoscopic molecular weight, benzene solution, formula weight 226.95 (observed molality, observed mol wt, association): 0.0846, 219, 0.96; 0.0642, 215, 0.95; 0.0439, 211, 0.93. Anal. Calcd for $\mathrm{C_9H_{17}GaO_2}$: C, 47.63; H, 7.55. Found: C, 47.52; H, 7.44. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ 4.94 (*H*-acac, 0.7 H), 1.63 (s, 6H, acac-C*H*$_3$), 1.28 (t, $J_{\mathrm{CH}} = 8$ Hz, 6H, $\mathrm{Ga{-}CH_2C}H_3$), 0.69 (q, $J_{\mathrm{CH}} = 8$ Hz, 4H, $\mathrm{Ga{-}C}H_2\mathrm{CH_3}$). ^{13}C NMR (125.7 MHz, $\mathrm{C_6D_6}$): δ 193.75 (s, −C=O), 100.78 (s, =C−), 27.35 (s, acac-$\mathrm{CH_3}$), 9.74 (s, $\mathrm{Ga{-}CH_2CH_3}$), 4.70 (s, $\mathrm{Ga{-}CH_2CH_3}$). IR (neat, cm^{-1}): 1587 (vs), 1525 (vs), 1417 (vs), 1370 (vs).

$\mathbf{Mes_2Ga(acac)}$. Yield of product: method A, 89.3%. Colorless solid. After the mesitylene was removed by holding the sample at 45 °C while dynamically pumping on the sample overnight, $\mathrm{Mes_2Ga(acac)}$ was purified by recrystallization from methylcyclohexane. Mp: 131.4 °C (onset of glass transition) to 138.7 °C (melting to clear liquid). Cryoscopic molecular weight, benzene solution, formula weight 407.20 (observed molality, observed mol wt, association): 0.0820, 382, 0.94; 0.0647, 374, 0.92; 0.0397, 388, 0.95. Anal. Calcd for $C_{23}H_{29}GaO_2$: C, 67.84; H, 7.18. Found: C, 67.82; H, 7.35. ^1H NMR (400 MHz, C_6D_6): δ 6.86 (s, 4 H, Mes-H), 4.92 (s, 0.7 H, *H*-acac), 2.60 (s, *o*-Mes-CH_3), 2.18 (s, 6H, *p*-Mes-CH_3), 1.52 (s, 6H, acac-CH_3). ^{13}C NMR (125.7 MHz, C_6D_6): δ 193.38 (s, C=O), 145.17 (s, Mes), 142.15 (s, Mes), 138.31 (s, Mes), 128.46 (s, Mes), 101.43 (s, =C−), 27.50 (s, acac-CH_3), 24.94 (s, *o*-Mes-CH_3), 21.61 (*p*-Mes-CH_3). IR (Nujol mull, cm^{-1}): 1577 (s), 1530 (s), 1459 (s), 1399 (m), 1373 (m), 1362 (m, sh), 1355 (m), 1345 (m).

Me_2Ga(tmhd). The colorless crystalline solid was isolated by holding the reaction mixture at −20 °C (alcohol/ice) while solvent was removed by vacuum distillation, and then the product was purified by room-temperature vacuum sublimation. Yield of product: method A, 95.9%. Mp: 24−25 °C. Vp at 20 °C: 0.7 mmHg. Cryoscopic molecular weight, benzene solution, formula weight 283.06 (observed molality, observed mol wt, association): 0.0757, 288, 1.02; 0.0608, 280, 0.99, 0.0401, 271, 0.96. Anal. Calcd for $C_{13}H_{25}GaO_2$: C, 55.16; H, 8.90. Found: C, 55.05; H, 8.86. ^1H NMR (500 MHz, C_6D_6): δ 5.72 (s, 0.7 H, tmhd-*H*), 1.06 (s, 18 H, tmhd-CH_3), 0.07 (s, 6 H, Ga−CH_3). ^{13}C NMR (125.7 MHz, C_6D_6): δ 203.70 (s, −C=O), 91.32 (s, =C−), 41.65 (s, tmhd-CCH_3), 28.33 (s, tmhd-CCH_3), −6.58 (s, Ga−CH_3). IR (neat, cm^{-1}): 1597 (m), 1571 (vs, sh), 1560 (vs, sh), 1554 (vs), 1538 (vs), 1501 (vs), 1459 (m), 1380 (vs), 1356 (vs).

Mes_2Ga(tmhd). Yield of product: method A, 75.5% based upon $GaMes_3$. The colorless solid was isolated after removing other volatile products and solvent by vacuum distillation for 8 h while holding sample at 55 °C; then it was recrystallized from methylcyclohexane at −30 °C. Mp: 152.0−155.4 °C (glass transition), 160.5−165.2 °C (melting to clear liquid). Cryoscopic molecular weight, benzene solution, formula weight 491.36 (observed molality, observed mol wt, association): 0.0780, 519, 1.06; 0.0573, 408, 0.83; 0.0381, 501, 1.02. Anal. Calcd for $C_{29}H_{41}GaO_2$: C, 70.89; H, 8.41. Found: C, 70.89; H, 8.43. ^1H NMR (500 MHz, C_6D_6): δ 6.85 (s, 4 H, Mes-*H*), 5.78 (s, 0.7 H, *H*-tmhd), 2.60 (s, 12H, *o*-Mes-CH_3), 2.18 (s, 6H, *p*-Mes-CH_3), 1.02 (s, 18 H, tmhd-CH_3). ^{13}C NMR (125.7 MHz, C_6D_6): δ 203.04 (s, C=O), 145.12 (s, Mes), 142.52(s, Mes), 138.21 (s, Mes), 128.44 (s, Mes), 92.18 (s, =C−), 41.69 (tmhd-CCH_3), 28.27 (s, tmhd-CCH_3), 25.02 (s, *o*-Mes-CH_3), 21.60 (*p*-Mes-CH_3). IR (Nujol mull, cm^{-1}): 1599 (m), 1552 (vs), 1508 (s), 1460 (vs), 1400 (m), 1375 (s) 1353 (s).

Reaction between $GaMe_3$ and $Ga(acac)_3$ in a 1:2 Mole Ratio. A Solv-Seal glass tube equipped with a magnetic stir bar was charged with 2.025 g (5.516 mmol) of $Ga(acac)_3$, 0.317 g (2.76 mmol) of $GaMe_3$, and 20 mL of pentane. Then the reaction mixture was heated with a 70 °C oil bath and stirred for 20 h. However, the presence of a slightly soluble colorless solid in the reaction mixture suggested that reaction was incomplete. Thus, approximately 20 mL of Et_2O was added and the resulting solution was heated with a 70 °C oil bath for 2 h. Vacuum distillation under dynamic vacuum with the original flask held at −20 °C and with traps on the vacuum line at −20 and −196 °C produced a mixture of a colorless crystalline solid and a slightly yellow (almost colorless) powdery solid in the Schlenk flask and a small amount of colorless crystals in the −20 °C trap. The pentane and ether collected in the −196 °C trap. The colorless crystals in the Schlenk flask and in the −20 °C trap were transferred at room temperature to a weighable tube on the vacuum line. The melting point of the crystals (22−23 °C) and subsequent ^1H and ^{13}C NMR spectra confirmed the presence of Me_2Ga(acac) (0.309 g, 1.55 mmol). ^1H NMR (500 MHz, C_6D_6): δ 4.93 (s, 0.3H, acac-*H*), 1.58 (s, 6 H, acac-CH_3), 0.03 (s, 6 H, Ga−CH_3). ^{13}C NMR (125.7 MHz, C_6D_6): δ 193.33 (C=O), 100.71 (=C−), 27.41 (acac-CH_3), −6.22 (Ga−CH_3). The powdery higher melting solid remaining in the Schlenk flask was identified as unreacted $Ga(acac)_3$ (1.360 g, 3.71 mmol; mp 197.0−199.5 °C (lit.[12] mp 194 °C)). ^1H NMR (500 MHz, C_6D_6): δ 5.17, 1.74.

Table 3. Data for the X-ray Crystallographic Studies of Mes_2Ga(hfac) and $Me_2Ga(hfac){\cdot}NC_5H_5$

compd	Mes_2Ga(hfac)	$Me_2Ga(hfac){\cdot}NC_5H_5$
mol formula	$C_{23}H_{23}F_6GaO_2$	$C_{12}H_{12}F_6GaNO_2$
cryst syst	orthorhombic	orthorhombic
space group	$Pna2_1$ (No. 33)	*Pbca* (No. 61)
a, Å	8.167(2)	8.0160(13)
b, Å	18.982(5)	18.755(4)
c, Å	15.345(4)	21.591(4)
V, Å^3	2378.9(10)	3246.1(11)
Z	4	8
mol wt	515.1	385.9
D, g/cm^3	1.438	1.579
μ(Mo Kα), mm^{-1}	1.212	1.750
T, max/min	N/A	0.4536/0.5240
F(000)	1048	1536
2θ range, deg	5−45	5−45
h	−8 to 0	0−8
k	0−20	0−20
l	0−16	−23 to +23
no. of rflns collected	1833	4727
no. of indep rflns	1635	2132 ($R_{int} = 3.7\%$)
no. of rflns above 6σ	909	1002
absolute structure	$\eta = 0.2(2)$	N/A
weighting scheme, w^{-1}	$\sigma^2(F) + 0.0017F^2$	$\sigma^2(F) + 0.0066F^2$
no. of params refined	296	200
final *R* indices (all data), %	$R = 8.78$, $R_w = 7.03$	$R = 6.33$, $R_w = 9.34$
R indices (6σ data), %	$R = 4.44$, $R_w = 4.71$	$R = 5.48$, $R_w = 6.53$
goodness of fit	1.00	0.98
largest and mean Δ/σ	0.003, 0.001	0.075, 0.005
data-to-param ratio	5.5:1	5.8:1
largest diff peak, e Å^{-3}	0.50	0.58
largest diff hole, e Å^{-3}	−0.41	−0.37

Reaction between $GaMes_3$ and H(hfac) in a 1:2 Mole Ratio (Neat). Trimesitylgallium (0.816 g, 1.91 mmol) and H(hfac) (0.808 g, 3.88 mmol) were combined in a Schlenk flask to form a bright yellow reaction mixture, which was stirred at room temperature for 12 h. Then, three products, a volatile colorless liquid (0.394 g, 3.28 mmol of mesitylene), a volatile colorless crystalline solid (0.429 g, 0.621 mmol of $Ga(hfac)_3$, mp 70.3−72.5 °C (lit.[12] mp 68.5−70.0 °C), and a relatively less volatile yellow solid (0.419 g, 0.815 mmol of Mes_2Ga(hfac), mp 89.6−94.1 °C) were separated by either vacuum distillation or sublimation, as appropriate, and identified by using the vacuuum line to determine the vapor pressure and molecular weight of the volatile liquid (mesitylene) and the melting points to identify the gallium-containing solids.

Collection of X-ray Diffraction Data. In each case crystals were sealed into thin-walled glass capillaries under an argon atmosphere inside a drybox kept under strictly anaerobic and moisture-free conditions. The crystals were inspected under a binocular polarizing microscope to ensure that they were single; they were then centered accurately on a Siemens R3m/V automated four-circle diffractometer. The unit cell parameters and Laue symmetry were determined as described previously.[28] Intensity data (Mo Kα, $\lambda = 0.710\ 730$ Å) were collected at ambient temperatures (24−25 °C) with graphite- monochromatized radiation. Data were corrected for absorption and for Lorentz and polarization factors. Details are provided in Table 3.

(**a**) **$Mes_2Ga(CF_3COCHCOCF_3)$**. The crystal had the dimensions 0.4 × 0.2 × 0.2 mm. The crystal belongs to the orthorhombic system (*mmm* diffraction symmetry); the systematic absences ($0kl$ for $k + l = 2n + 1$, $h0l$ for $h = 2n$) are consistent with either the centrosymmetric space group *Pnam*

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[28] Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

or the noncentrosymmetric space group $Pna2_1$. The successful solution of the structure was carried out in the lower, acentric, space group.

(b) $Me_2Ga(CF_3COCHCOCF_3)(py)$. The crystal had the dimensions 0.6 × 0.2 × 0.2 mm and belongs to the orthorhombic crystal system. The systematic absences ($0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$) uniquely define the centrosymmetric space group *Pbca*.

Determination of the Crystal Structures. All crystallographic calculations were carried out on a VAXstation 3100 computer with use of the Siemens SHELXTL PLUS (Release 4.11 (VMS)) program package.[29] The scattering factors used were the analytical values for neutral atoms; these were corrected for both components ($\Delta f'$ and $i\Delta f''$) of anomalous dispersion.[30] The structures were solved by direct methods and difference Fourier syntheses. All non-hydrogen atoms were located, and their positional and anisotropic thermal parameters were refined. Hydrogen atoms were included in calculated positions based upon d(C−H) = 0.96 Å and the appropriate idealized trigonal or tetrahedral geometry.[31] The correctness of each structure was confirmed by means of a final difference Fourier synthesis.

Acknowledgment. This work was supported in part by the Office of Naval Research (O.T.B.). The upgrading of the X-ray diffractometer was made possible by Grant 89-13733 from the Chemical Instrumentation Program of the National Science Foundation.

Supporting Information Available: Complete tables of positional parameters, interatomic distances and angles, anisotropic thermal parameters, and calculated positions for hydrogen atoms for each compound (7 pages). Ordering information is given on any current masthead page.

OM970988E

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[29] Sheldrick, G. M. SHELXTL PLUS, Release 4.11 (VMS); Siemens Analytical Instrument Corp., Madison, WI, 1989.

[30] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99−101, 149−150.

[31] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.