

Syntheses, Characterization, and X-ray Crystal Structures of β -Diketiminate Group 13 Hydrides, Chlorides, and Fluorides

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A series of organometallic compounds of group 13 metals supported by the sterically encumbered β -diketiminate ligand containing hydrides, fluorides, chlorides, and bromide have been synthesized and structurally characterized. The synthetic strategy applied utilizes halide metathesis and reduction of metal chlorides to the corresponding hydrides. Thus, the reaction of LLi•OEt₂ with MeMCl₂ affords LM(Me)Cl (M = Al (1), Ga (2), In (3)) and LGaBr₂ (4) with GaBr₃. Reduction of LGa(Me)Cl with LiH•BEt₃ leads to the formation of LGa(Me)H (10). Synthesis of LGaH₂ (12) has been accomplished by reacting LGal₂ (8) with LiH•BEt₃. LAI(Me)Cl (1) and LAIH₂ (6) have been converted to LAI(Me)F (5) and LAIF₂ (7), respectively. The former was obtained in a reaction of LGal₂ (8) with Me₃SnF while the latter was isolated in a reaction of LAIH₂ with BF₃•OEt₂. Similarly reaction of LGal₂ (8) with Me₃SnF affords LGaF₂ (9). Compounds reported herein have been characterized by elemental analyses, IR, NMR, EI-MS, and single-crystal X-ray diffraction techniques.

Introduction

Sterically encumbered β -diketiminate ligands offer a negative, bidentate chelating mode^{1,2} to a wide range of transition metals,^{2–7} main group elements,^{8–13} and lanthanide systems.¹⁴ A noticeable point is the ability of these ligands

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to stabilize low coordination numbers at the metal centers, rare coordination geometries, or low oxidation states owing to their ability to tune properly between the steric and electronic factors.^{6,7,12,13} Some of these complexes act as olefin polymerization catalysts,^{3,4,8,9,15} as models for active sites in metalloproteins,^{6,7} and also as complexes with unusual chemical properties.¹²

A number of M(III) derivatives with the β -diketiminate ligand L have been previously reported and structurally characterized [L = HC{(CMe)(2,6-*i*Pr₂C₆H₃N)}₂]. These include the cation [LAIMe]^{+,9} the dimethyl derivative LMMe₂,^{9,10} the dichloride LMCl₂, and the diiodide LMI₂ (M = Al, Ga, or In).¹⁶ Synthesis of LAIMe₂¹⁰ was reported by Smith et al. whereas other complexes were reported by Power and co-workers.¹⁶ Preparation of LMCl₂ was accomplished by the reaction of LLi•OEt₂ with MCl₃.¹⁶ Reaction of "GaI" with LLi•OEt₂ yields LGaI₂ and LGa,¹⁶ whereas LInI₂ was prepared by the reaction of LLi•OEt₂ with InI₃.¹⁶ LAIMe₂¹⁰ and LGaMe₂¹⁶ were isolated by the reaction of the corresponding trimethyls with the LH. LInMe₂ was prepared by

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Scheme 1. Preparation of Group 13 Methyl Chlorides Supported by the β -Diketiminate Ligand



the metathesis of LInCl₂ with 2 equiv of MeMgBr.¹⁶ It is noticeable that all these complexes have symmetrical substituents around the metal atom. Presently, there is a growing interest in the chemistry of such complexes where the metal atom has at least two different substituents.

On the basis of our longstanding interest in the synthesis of β -diketiminate complexes of group 13 metals, we have contributed to a whole new range of compounds.¹⁷⁻²⁵ Some of these are useful catalysts,^{23,25} compounds with syntheti-cally useful functional groups,^{17–21,23–25} and compounds with the metal in a low oxidation state.¹² We have reported recently that the sterically encumbered neutral LAI(Me)Cl can be utilized as a starting material to prepare the monohydroxide LAl(Me)OH, which in turn can again be used as a synthon to assemble a range of homo- and heterobimetallic derivatives²³⁻²⁵ some of which have found applications in ethylene polymerization²³ and polymerization of ϵ -caprolactone.²⁵ Therefore, it was our primary interest to prepare other derivatives of LAI(Me)Cl where the Al atom will have at least two different substituents and also to extend it to the congeners of group 13.

Results and Discussion

Synthesis of LM(Me)Cl (M = Al (1), Ga (2), In (3)) has been accomplished by the reaction of LLi•OEt₂ with MeMCl₂ (Scheme 1). It was observed that the reaction of LH with Me₂MCl leads to a mixture of products which are difficult to separate. Compounds 1-3 are examples of novel β -diketiminate metal complexes which are X-ray structurally characterized with metals having two different substituents. Spectroscopic properties of LAI(Me)Cl have already been reported.²⁶ Compounds LGa(Me)Cl (2) and LIn(Me)Cl (3)

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Scheme 3. Preparation of the β -Diketiminate Methylaluminum Fluoride



are thermally stable solids with melting points of 190 and 185 °C, respectively, and are sensitive to moisture. ¹H NMR of 2 reveals the Ga-Me to resonate at δ -0.31 ppm and two septets at δ 3.15 and 3.87 ppm corresponding to the CH protons of the *i*Pr moieties of the ligand, characteristics of asymmetrically substituted metal center in complexes with the β -diketiminate ligand. The corresponding protons of **3** appear at δ -0.28 ppm, and septets, at δ 3.15 and 3.83 ppm. The most intense peak in the EI-MS spectra of 2 and 3 corresponds to the loss of one Me group from the molecular ion and was observed at m/z 523 and 567, respectively. LGaBr₂ (4) was synthesized by the reaction of $LLi \cdot OEt_2$ with GaBr₃ in diethyl ether (Scheme 2). LGaBr₂ (4) melts at 236 °C. The base peak in the EI-MS spectrum of 4 at m/z 567 corresponds to the loss of one bromine atom from 4. Moreover, the molecular ion was observed at m/z 646 albeit in low intensity.

Trimethyltin fluoride has proved to be a versatile fluorinating agent particularly in the conversion of groups 4-6and also main group chlorides to the corresponding fluorides.²⁷⁻²⁹ Trimethyltin chloride generated during the metathesis is readily removed in vacuo. Thus, the reaction of LAl(Me)Cl (1) with Me₃SnF in THF results in the complete conversion of 1 to LAl(Me)F (5) (Scheme 3) which was characterized by its ¹⁹F NMR where the Al-F resonates at δ 8.6 ppm. Methyl protons of Al-*Me* are coupled to the F atom and are observed as a doublet (δ -0.82 ppm). EI-MS of 5 exhibits $[M^+ - Me]$ as the base peak at m/z 463.

When $LAlH_2$ (6) was treated with $BF_3 \cdot OEt_2$ at low temperature and allowed to warm to room temperature, the difluoride derivative LAIF₂ (7) was isolated (Scheme 4). A singlet in the ¹⁹F NMR of 7 (δ 6.8 ppm) confirms the formation of Al–F bonds. The EI-MS spectrum shows [M⁺] as the base peak at m/z 482. The corresponding gallium

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Scheme 4. Preparation of the β -Diketiminate Aluminum Difluoride



Scheme 5. Preparation of β -Diketiminate-Supported Gallium Difluoride



compound LGaF₂ (9) was synthesized by the reaction of LGaI₂ (8) with Me₃SnF (Scheme 5). ¹⁹F NMR of 9 exhibits the Ga-*F* to resonate at δ 38.3 ppm. The mass spectrum of 9 reveals the base peak as [M⁺ - F] at *m*/*z* 505 and the molecular ion at *m*/*z* 523 [M⁺] in low intensity.

A number of hydrides of aluminum have been prepared ranging from mono-,^{30,33} di-,³⁰⁻³⁴ and trihydrides.³⁵⁻³⁸ The latter has been a very strong and useful reducing agent in the form of alane and aluminates. The corresponding gallium compounds^{33,38,39} are also known but their stability is lower than the aluminum derivatives. Attempts have been devoted to increase the stability of these compounds by coordination of an ancillary ligand to the gallium atom. These are among the most easily accessible, more stable, and, usually, more malleable than the parent hydrides.^{33,39,40} Most common are the Lewis base adducts of group 13 metal hydrides.^{38,41} Thus, GaH₃•NMe₃ is stable below room temperature but its shelf life is considerably lower at room temperature. Therefore, it is a synthetic challenge to prepare stable mono- and dihydrides of gallium. An obvious route is the reduction of the corresponding chlorides with a suitable reducing agent.⁴²

The reduction of LGa(Me)Cl with LiH•BEt₃ in toluene smoothly affords LGa(Me)H (**10**) in good yield (Scheme 6).

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Scheme 6. Preparation of the β -Diketiminate Gallium Methyl Hydride







On the contrary reaction of LiH•BEt₃ with LAl(Me)Cl (1) affords a mixture of products which could not be separated and characterized. Other attempts to prepare LAl(Me)H (11) including reaction of LH with MeAlH₂•NMe₃⁴³ or reduction of LAl(Me)Cl (1) with LiAlH₄ were not successful. Compound **10** is a stable solid with a melting point of 177 °C. In the ¹H NMR spectrum of **10** Ga–*Me* protons resonate at δ 5.49 ppm as a broad signal, whereas the base peak in the EI-MS spectrum of **10** at *m*/*z* 487 corresponds to [M⁺ – Me]. The IR spectrum of **10** shows a strong band at $\tilde{\nu}$ 1825 cm⁻¹ which can be attributed to the Ga–H stretching frequency.

Similarly, the synthesis of dihydride of gallium LGaH₂ (12) involves the conversion of LGaI₂ (8) to LGaH₂ with LiH•BEt₃ (Scheme 7). In the ¹H NMR spectrum the Ga-*H* resonates at δ 4.58 ppm. The IR spectrum of 12 shows two strong bands at $\tilde{\nu}$ 1893 and 1861 cm⁻¹ which can be attributed to the asymmetric and symmetric stretch of the Ga-H bonds, respectively. The EI-MS spectrum exhibits the base peak at *m*/*z* 487, which corresponds to [M⁺ - H].

X-ray Structural Characterization of Complexes 1–5, 7, 9, 10, and 12. All complexes 1–5, 7, 9, 10, and 12 crystallize in the monoclinic system in $P2_1/n$ (1–4, 7, 9, and 12) or in $P2_1/c$ (5 and 10) with one molecule in the asymmetric unit. These compounds can be divided into three groups containing isomorphic species. The first group contains complexes 1–4 (two approximately similar substituents are attached to the metal center), the second include compounds 7, 9, and 12 (two small atoms (H or F) bound to the metal center), and the species 5 and 10 belong to the third one (two substituents with different size on the metal atom), respectively. Molecular structures of these complexes are depicted in Figures 1–9, respectively. The crystal data and structure refinement details of all complexes are summarized in Table 1, and selected bond lengths and angles

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Figure 1. Molecular structure of LAl(Me)Cl (1) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.



Figure 2. Molecular structure of LGa(Me)Cl (2) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.



Figure 3. Molecular structure of LIn(Me)Cl (3) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

are listed in Tables 2–4. The most common feature among the structures is that the four atoms C(1), C(3), N(1), and N(2) are almost coplanar, whereas the position of the metal and C(2) atoms depends strongly on the substituents attached to the metal center. If the substituents are small (H, F or electron lone pair), the C₃N₂M ring is planar or nearly planar (observed in LA1,¹² LA1H₂,³⁷ **7**, **9**, and **12**), and an elongation of the anisotropic displacement parameter perpendicular to the plane of the metal and the substituents is observed indicating vibration perpendicular to the plane but larger substituents attached to the metal atom cause its significant deviation out of the plane. The C(2) atom is in this case also deviated from the C₂N₂ plane, but the deviation is not so large as in the case of the metal center. This boat



Figure 4. Molecular structure of LGaBr₂ (**4**) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.



Figure 5. Molecular structure of LAl(Me)F (5) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.



Figure 6. Molecular structure of $LAlF_2$ (7) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

conformation of the C_3N_2M ring can also be found in many other derivatives of these ligands from group 13 metals and from different elements of the periodic table. In the complexes **1**–**5**, **7**, **9**, **10**, and **12** the C–C and C–N distances of the C_3N_2M ring lie within the narrow ranges 1.394–1.410 and 1.325–1.346 Å, respectively, which are indicative of considerable multiple bond character and delocalization in these bonds. It is noteworthy that within the C_3N_2M (M = Al, Ga, In) rings the N–M–N angle is invariably the narrowest, smallest for LIn(Me)Cl (**3**) at 90.9(1)° and widest for LGaF₂ (**9**) at 100.8(1)°, depending on the covalent radii



Figure 7. Molecular structure of $LGaF_2$ (9) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.



Figure 8. Molecular structure of LGa(Me)H (10) with 50% thermal ellipsoids. All hydrogen atoms except that on Ga(1) are omitted for clarity.



Figure 9. Molecular structure of $LGaH_2$ (12) with 50% thermal ellipsoids. All hydrogen atoms except those on Ga(1) are omitted for clarity.

of the metal and on the size of the substituents, respectively. In all complexes, the substituents are coordinated to the metal atom in the form of distorted tetrahedron.

In complexes 1-3 the metal atoms are surrounded by the chlorine atom, methyl group, and nitrogen atoms of the chelating β -diketiminate ligand (Figures 1–3). The bite angles of the β -diketiminate ligands N(1)–M(1)–N(2), which are 97.6(1), 97.1(1), and 90.9(1)° for 1–3, respectively, are smaller than the regular tetrahedral bond angles (109.28°) and follow the trend in the size of covalent radii

Table 1. Crystallographic	Data and Structure F	Refinement for Comp.	lexes 1-5, 7, 10, and	d 12					
param	1	7	3	4	S	7	6	10	12
formula	C ₃₀ H ₄₄ AlCIN ₂	C ₃₀ H ₄₄ ClGaN ₂	C ₃₀ H ₄₄ ClInN ₂	C ₂₉ H ₄₁ Br ₂ GaN 2	C ₃₀ H ₄₄ AlFN ₂	$C_{29}H_{41}AIF_2N_2$	$C_{29}H_{41}F_2GaN_2$	C ₃₀ H ₄₅ GaN ₂	C ₂₉ H ₄₃ GaN ₂
fw	495.10	537.84	582.94	647.18	478.65	482.62	525.36	503.40	489.37
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_{1/n}$	$P2_{1/n}$	$P2_{1}/n$	$P2_{1/n}$	$P2_{1/c}$	$P2_{1}/n$	$P2_{1/n}$	$P2_{1/c}$	$P2_{1/n}$
temp, K	100(2)	100(2)	100(2)	133(2)	100(2)	103(2)	133(2)	100(2)	133(2)
$\lambda, \tilde{\lambda}$	1.541 78	1.541 78	1.541 78	0.710 73	1.541 78	1.541 78	0.710 73	1.541 78	0.710 73
a, Å	12.620(3)	12.666(3)	12.789(2)	12.685(2)	9.002(2)	12.474(3)	12.500(2)	8.957(2)	12.508(2)
b, Å	19.323(4)	19.287(4)	19.631(3)	19.729(2)	9.622(2)	15.853(3)	15.869(2)	9.664(2)	16.188(2)
$c, m \AA$	13.305(3)	13.299(3)	13.294(2)	13.321(2)	32.954(7)	14.196(3)	14.285(2)	33.123(6)	14.095(2)
β , deg	117.29(3)	117.55(3)	117.53(1)	117.43(2)	91.59(3)	104.39(3)	104.50(2)	91.43(2)	105.06(2)
V, Å ³	2883(1)	2880(1)	2960(1)	2958.9(7)	2853(1)	2719(1)	2743.4(7)	2866(1)	2755.9(7)
Z	4	4	4	4	4	4	4	4	4
$ ho_{ m caled}, { m g/cm}^3$	1.141	1.240	1.308	1.453	1.114	1.179	1.272	1.167	1.179
u, mm^{-1}	1.600	2.292	7.340	3.650	0.812	0.911	1.035	1.432	1.016
F(000)	1072	1144	1216	1320	1040	1040	1112	1080	1048
cryst size, mm ³	$0.20 \times 0.20 \times 0.10$	$0.10 \times 0.10 \times 0.07$	$0.10 \times 0.10 \times 0.05$	$0.30 \times 0.30 \times 0.20$	$0.20 \times 0.10 \times 0.10$	$0.60 \times 0.50 \times 0.50$	$0.20 \times 0.20 \times 0.20$	$0.30 \times 0.30 \times 0.20$	$0.30 \times 0.30 \times 0.20$
θ range for data collen, deg	4.00 - 58.99	3.99 - 59.09	3.97 - 59.04	1.84 - 24.84	2.68 - 58.95	4.23 - 59.09	1.94 - 24.82	2.67 - 58.95	1.94 - 24.79
no. of reflcns colled	23769	16011	15305	16490	11809	24658	40901	17143	38900
no. of indent reflcns (Rint)	4096 (0.0386)	4108(0.0235)	4134(0.0344)	5068 (0.0707)	3966 (0.0300)	3916 (0.0462)	4709 (0.0688)	4090(0.0310)	4716 (0.0630)
no. of data/restraints/params	4096/3/327	4108/0/322	4134/0/322	5068/0/318	3966/0/322	3912/0/321	4709/0/318	4090/0/316	4716/1/307
GOF on F^2	1.048	1.047	1.070	1.036	1.038	1.015	0.977	1.062	1.033
$\mathrm{R1}^{,a}$ w $\mathrm{R2}^{b}$ $(I > 2\sigma(I))$	0.0357, 0.0917	0.0228, 0.0618	0.0215, 0.0537	0.0359, 0.0928	0.0336, 0.0861	0.0328, 0.0809	0.0332, 0.0683	0.0285, 0.0704	0.0292, 0.0668
$R1,^a wR2^b$ (all data)	0.0445, 0.0977	0.0231, 0.0620	0.0218, 0.0540	0.0421, 0.0960	0.0384, 0.0894	0.0404, 0.0859	0.0537, 0.0724	0.0288, 0.0707	0.0390, 0.0698
largest diff peak/hole, e•Å ⁻³	0.194 / -0.335	0.293/-0.270	0.382/-0.373	1.412 / -0.882	0.245/-0.210	0.194 / -0.219	0.418 / -0.333	0.609/-0.231	0.223/-0.344
$^{a}\mathrm{R}1=\Sigma F_{\mathrm{o}} - F_{\mathrm{c}} /\Sigma $	$F_{\rm o} .\ ^b$ wR2 = [$\Sigma w(H)$	$F_{\rm o}^{2} - F_{\rm c}^{2})^{2}/\sum w F_{\rm o}^{2} $	[²] ^{1/2} .						

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds $1-4^{a}$

param	1	2	3	4
M(1)-Cl(1)	2.158(1)	2.223(1)	2.402(1)	
M(1) - Br(1)				2.286(1)
M(1) - Br(2)				2.330(1)
M(1) - C(6)	1.905(5)	1.956(2)	2.138(2)	
M(1) - N(1)	1.906(2)	1.949(1)	2.148(2)	1.925(3)
M(1)-N(2)	1.887(2)	1.936(1)	2.133(2)	1.908(2)
Cl(1)-M(1)-C(6)	114.9(4)	114.5(1)	119.1(1)	
Br(1) - M(1) - Br(2)				112.2(1)
N(1)-M(1)-N(2)	97.6(1)	97.1(1)	90.9(1)	99.8(1)
N(1)-M(1)-Cl(1)	105.4(1)	103.1(1)	100.9(1)	
N(1)-M(1)-Br(1)				116.0(1)
N(1)-M(1)-Br(2)				107.2(1)
N(1)-M(1)-C(6)	117.2(4)	119.3(1)	122.4(1)	
N(2)-M(1)-Cl(1)	106.8(1)	104.0(1)	101.3(1)	
N(2)-M(1)-Br(1)				112.9(1)
N(2)-M(1)-Br(2)				107.9(1)
N(2)-M(1)-C(6)	113.2(4)	116.3(1)	117.0(1)	

 a M = Al (1), Ga (2, 4), In (3).

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds 5, 7, and 9

param	5	7	9
M(1) - F(1)	1.679(1)	1.655(1)	1.773(2)
M(1) - F(2)		1.650(1)	1.755(2)
M(1) - C(6)	1.944(2)		
M(1) - N(1)	1.897(1)	1.865(1)	1.895(2)
M(1)-N(2)	1.885(1)	1.866(1)	1.899(2)
F(1) - M(1) - C(6)	144.7(1)		
F(1) - M(1) - F(2)		107.8(1)	103.7(1)
N(1)-M(1)-N(2)	97.1(1)	99.3(1)	100.8(1)
N(1)-M(1)-F(1)	105.7(1)	112.1(1)	114.0(1)
N(1)-M(1)-F(2)		113.2(1)	111.9(1)
N(1)-M(1)-C(6)	115.8(1)		
N(2)-M(1)-F(1)	107.8(1)	112.8(1)	112.4(1)
N(2)-M(1)-F(2)		111.6(1)	114.5(1)
N(2)-M(1)-C(6)	114.1(1)		

 a M = Al (5, 7), Ga (9).

Table 4. Selected Bond Distances (Å) and Angles (deg) for Compounds 10 and 12

param	10	12
Ga(1) - H(1)	1.75(2)	1.54(2)
Ga(1)-H(2)		1.52(2)
Ga(1) - C(6)	1.955(2)	
Ga(1)-N(1)	1.968(2)	1.960(1)
Ga(1)-N(2)	1.976(2)	1.963(1)
H(1)-Ga(1)-H(2)		118(1)
H(1)-Ga(1)-C(6)	118.3(6)	
N(1)-Ga(1)-N(2)	94.3(1)	95.7(1)
N(1)-Ga(1)-C(6)	111.2(1)	
N(2)-Ga(1)-C(6)	112.7(1)	
N(1)-Ga(1)-H(1)	109.5(6)	110.7(8)
N(1)-Ga(1)-H(2)		109.0(9)
N(2)-Ga(1)-H(1)	108.3(7)	110.2(8)
N(2)-Ga(1)-H(2)		110.4(9)

for these metals (1.35 Al, 1.22 Ga, 1.63 Å In).44 The Al-(1)-Cl(1) bond length (2.158(1) Å) in **1** is similar to that found in LAICl₂ (2.134(1) and 2.119(1) Å, average 2.126 Å).¹⁶ The C(6)-Al(1)-Cl(1) angle $114.9(4)^{\circ}$ lies between the angles of C(1)-Al(1)-C(2) $115.4(2)^{\circ}$ in LAIMe₂¹⁰ and Cl(1)-Al(1)-Cl(2) 108.0(1)° in LAlCl₂ (Table 2).¹⁶

The Ga(1)-C(6) bond length in LGa(Me)Cl (2) (1.956-(2) Å) is comparable to that observed in LGaMe₂ (1.970(2))and 1.979(2) Å, average 1.975 Å).¹⁶ Similarly, the Ga(1)-

Cl(1) bond length in 2 is 2.223(1) Å, which is the same as that found in LGaCl₂ (2.228(1) and 2.218(1) Å, average 2.223 Å).¹⁶ The C(6)–Ga(1)–Cl(1) angle is 114.5(1)° (Table 2), which lies between the angles of C(30)-Ga(1)-C(31)at $122.44(9)^{\circ}$ in LGaMe₂¹⁶ and Cl(1)-Ga(1)-Cl(2) at 110.20(4)° in LGaCl₂.16

The In(1)-C(6) bond length in LIn(Me)Cl (3) (2.138(2)) Å) is almost similar to those observed in $LIn(Me)_2$ (2.148-(1) and 2.168(1) Å, average 2.158 Å).¹⁶ The In(1)-Cl(1) bond length (2.402(1) Å) is comparable to that of LInCl₂ (2.387(1) and 2.404(3) Å, average 2.396 Å).¹⁶ The C(6)-In(1)-Cl(1) angle is 119.1(1)° (Table 2), which is wider than the Cl(1)–In(1)–Cl(2) 108.99(8)° in LInCl₂¹⁶ but narrower than the C(30)-In(1)-C(31) 130.94(6)° in LInMe₂.¹⁶

The molecular structure of LGaBr₂ (4) has also been determined by single-crystal X-ray techniques. A perspective view of the molecular structure of 4 is shown in Figure 4, and relevant bond lengths and angles are listed in Table 2. The Ga-Br bond lengths (2.286(1) and 2.330(1) Å) are shorter than those found in [PyGaBr₂]₂ (2.350(2) Å)⁴⁵ and tBu₃SiGaBr₂•THF (2.360(1) Å)⁴⁶ and [(3,5-Me₂C₆H₃CH₂)₂- $GaBr_2$ (average 2.519 Å).⁴⁷ The Br(1)-Ga(1)-Br(2) angle is 112.2(1)° and is considerably wider than the corresponding angles in [PyGaBr₂]₂ (105.8(1)°)⁴⁵ and tBu₃SiGaBr₂•THF $(105.6(1)^{\circ})^{46}$ and $[(3,5-Me_2C_6H_3CH_2)_2GaBr_2]_2$ (92.1(1)°).⁴⁷ The N(1)-Ga(1)-N(2) angle within the chelating ring of the β -diketiminate ligand is 99.8(1)°, which is slightly wider than that found in LGa(Me)Cl $(97.1(1)^{\circ})$.

The Al(1)-C(6) bond distance in LAl(Me)F (5) (1.944-(2) Å) is slightly shorter than that found in LAlMe₂ (average 1.964 Å).¹⁰ The Al-F bond length (1.679(1) Å) is slightly longer than that observed in $LAIF_2(7)$ (1.656(1) and 1.650-(1) Å) and identical in $[OCMeCHCMeN(2.6-iPr_2C_6H_3)]_2AIF$ (1.678(1) Å).⁴⁸ However, the Al-F bond lengths in **5** and **7** are typical for terminal bonds and are comparable to terminal Al-F bonds in [{ $(Me_3Si)_3CAlF_2$ }] (average 1.669 Å) but are significantly shorter than the bridging ones (average 1.805 Å).⁴⁹ F(1)-Al(1)-C(6) angle in **5** is $144.7(1)^{\circ}$, which is wider than the F(1)-Al(1)-F(2) angle of $107.8(1)^{\circ}$ in 7, probably due to the smaller size of the F atom compared to that of the Me group. Ga-F distances observed in LGaF₂ (9) are 1.755(2) and 1.773(2) Å, which are considerably shorter than those found in Ga(pc)F (1.936(1) Å) (pc = phthalocyanato),⁵⁰ [Mes₂Ga(F)(tBuNH₂)] (1.838(3) Å)⁵¹ $[{(Me_3Si)_2HC}_2GaF]_2$ (average 1.966 Å),⁵² and $[Mes_2GaF]_2$ $(1.947(2) \text{ Å}).^{53}$ The F(1)-Ga(1)-F(2) angle in 9 is 103.7-(1)°, which is identical with the average F-Ga-F bond angle

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β -Diketiminate Group 13 Hydrides and Halides

in [{(Me₃Si)₂HC}₂GaF]₂⁵² but wider than that observed in [Mes₂GaF]₂ (78.9(1)°).⁵³ The N(1)–Ga(1)–N(2) angle within the C₃N₂Ga ring in **9** is 100.8(1)°, which is wider than the similar angles found in LGa(Me)Cl (**2**) (97.1(1)°) but comparable to that observed in LGaBr₂ (**4**) (99.8(1)°).

The structures of the complexes LGa(Me)H (10) and LGaH₂ (12) are analogous to their parent compounds LGa-(Me)Cl (2) and LGaI₂, respectively. The Ga(1)–C(6) bond length in LGa(Me)H (10) (1.955(2) Å) was found to be identical with 1.956(2) Å observed in LGa(Me)Cl (2). The Ga–H distances in 12 (1.54(2) and 1.52(2) Å) are shorter than in 10 but are in agreement with Ga–H distances reported earlier, for example in $[(tBuO)_2GaH)]_2$ (1.53(7) Å).⁵⁴ Furthermore, there is a residual density peak (0.61 e.Å⁻³) close to the hydrogen of 10 caused by an unmodeled disorder (either ca. 6% methyl or 3.5% chlorine). This leads to an artificial elongation of the Ga–H bond.

Conclusion

Herein, we have described the syntheses and X-ray structures of group 13 hydrides, chlorides, bromide, and fluorides supported by a β -diketiminate ligand. This procedure utilizes the reaction of metal chlorides with super hydride to prepare metal hydride and reaction of metal chlorides with Me₃SnF or BF₃•OEt₂ to prepare metal fluorides. The resulting compounds are excellent starting materials and can be used to prepare interesting compounds; an example has already been demonstrated in preparing terminal hydroxides of Al²³ and Ga²⁰ as well as in the synthesis of tetranuclear alumoxane hydride and alumoxane gallium hydride.²⁴ Similarly we anticipate that other derivatives reported here would allow further elaboration of these synthons.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Samples prepared for spectral measurements as well as for reactions were manipulated in a glovebox. Solvents were dried using conventional procedures, distilled under nitrogen, and degassed prior to use. Deuterated NMR solvents were treated with Na/K alloy, distilled, and stored under nitrogen. MeGaCl₂,⁵⁵ MeInCl₂,⁵⁶ LH,³ LLi•OEt₂,⁵⁷ LGaCl₂,¹⁶ LGaI₂,¹⁶ MeAlH₂•NMe₃,⁴³ and Me₃SnF⁵⁸ were prepared as described in the literature. MeAlCl₂, BF₃•OEt₂, and LiH•BEt₃ were purchased from Aldrich and were used without purification.

Physical Measurements. The ¹H NMR spectra were recorded on Bruker AM 200 NMR spectrometer with SiMe₄ as external

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standard, and ¹⁹F NMR spectra were recorded with C_6F_6 as external standard. Mass spectra were recorded on a Finnigan MAT 8230 mass spectrometer using the EI-MS method. The most intense peak of an isotopic distribution is tabulated. IR spectra were recorded on Bio-Rad Digilab FTS-7 spectrometer as a Nujol mull between KBr plates. Melting points were obtained in sealed capillaries on a Büchi B540 instrument. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

Synthesis of LGa(Me)Cl (2). LLi·OEt₂ (1.49 g, 3.00 mmol) dissolved in toluene (30 mL) was cooled to -78 °C, and MeGaCl₂ (0.47 g, 3.00 mmol) dissolved in toluene (20 mL) was added with continuous stirring. The solution was allowed to warm to room temperature and stirred overnight. After removal of all volatiles, the residue was extracted with *n*-hexane (50 mL). Partial removal of the solvent and storage at -26 °C afforded colorless crystals of LGa(Me)Cl. An additional crop of LGa(Me)Cl was obtained from the mother liquor. Total yield: 1.26 g (78%). Mp: 190 °C. Anal. Calcd for $C_{30}H_{44}ClGaN_2$ ($M_r = 537.86$): C, 66.99; H, 8.25; N, 5.21. Found: C, 66.87; H, 8.32; N, 5.18. ¹H NMR (C₆D₆, 200 MHz): $\delta -0.31$ (s, 3 H, GaMe), 1.04 (d, 6 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 1.19 (two overlapped d, 12 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 1.48 (d, 6 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 1.57 (s, 6 H, CMe), 3.15 (sept, 2 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 3.87 (sept, 2 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 4.90 (s, 1 H, γ-CH), 7.01-7.14 (m, 6 H, Ar). MS [EI; m/z (%)]: 538 (12) [M⁺], 523 (100) [M⁺ – Me], 501 (34) $[M^+ - Cl]$, 485 (14) $[M^+ - Me - Cl]$. IR (Nujol, cm⁻¹): $\tilde{\nu}$ 1532, 1468, 1441, 1385, 1302, 1262, 1179, 1100, 1056, 1023, 934, 872, 797, 778, 759, 726, 646, 584, 532, 450.

Synthesis of LIn(Me)Cl (3). The preparation of LIn(Me)Cl was carried out by using a procedure similar to that for LGa(Me)Cl. The quantities of the reactants used are 1.00 g (2.00 mmol) for LLi•OEt₂ and 0.40 g (2.00 mmol) for MeInCl₂. Yield: 0.75 g (65%). Mp: 185 °C. Anal. Calcd for C₃₀H₄₄ClInN₂ ($M_r = 582.95$): C, 61.81; H, 7.61; N, 4.81. Found: C, 61.79; H, 7.58; N, 4.82. ¹H NMR (C₆D₆, 200 MHz): δ –0.28 (s, 3 H, In*Me*), 1.09 (d, 6 H, $J_{H-H} = 6.8$ Hz, CH*Me*₂), 1.23 (two overlapped d, 12 H, $J_{H-H} = 6.8$ Hz, CH*Me*₂), 1.46 (d, 6 H, $J_{H-H} = 6.8$ Hz, CH*Me*₂), 3.83 (sept, 2 H, $J_{H-H} = 6.8$ Hz, CH*Me*₂), 4.80 (s, 1 H, γ -CH), 7.10–7.14 (m, 6 H, *Ar*). MS [EI; m/z (%)]: 582 (12) [M⁺], 567 (100) [M⁺ – Me]. IR (Nujol, cm⁻¹): $\tilde{\nu}$ 1526, 1383, 1317, 1268, 1254, 1177, 1163, 1107, 1099, 1055, 1043, 1021, 933, 859, 796, 778, 758, 720, 635, 518, 446.

Synthesis of LGaBr₂ (4). GaBr₃ (1.00 g, 3.23 mmol) dissolved in diethyl ether (40 mL) was cooled to -78 °C, and a solution of LLi•Et₂O (1.61 g, 3.23 mmol), dissolved in diethyl ether and cooled to -78 °C was added. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. After removal of all volatiles, 4 was extracted with *n*-hexane (50 mL). After removal of *n*-hexane, 4 was dissolved in diethyl ether and colorless crystals were obtained at -27 °C. Yield: 1.71 g (82%). Mp: 236 °C. Anal. Calcd for $C_{29}H_{41}Br_2GaN_2$ ($M_r = 647.18$): C, 53.82; H, 6.39; Br, 24.69; Ga, 10.77; N, 4.33. Found: C, 53.91; H, 6.42; Br, 24.32; Ga, 10.53, N, 4.39. ¹H NMR (200 MHz, CDCl₃): δ 1.20 (d, 12 H, $J_{\rm H-H} = 6.8$ Hz, CHMe₂), 1.31 (d, 12 H, $J_{\rm H-H} = 6.8$ Hz, CHMe₂), 1.90 (s, 6 H, CMe), 3.37 (sept, 4 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 5.31 (s, 1 H, γ-CH), 7.20-7.30 (m, 6 H, Ar). MS [EI; m/z (%)]: 646 (38) [M⁺], 567 (100) [M⁺ – Br], 486 (7) [M⁺ – 2Br]. IR (Nujol, cm⁻¹): $\tilde{\nu}$ 1877, 1654, 1522, 1261, 1149, 1099, 1021, 934, 875, 799, 722, 638, 535.

Synthesis of LAI(Me)F (5). THF (40 mL) was added to a mixture of LAI(Me)Cl (0.99 g, 2.00 mmol) and Me₃SnF (0.37 g,

2.00 mmol). The mixture was then stirred at room temperature until a clear solution was obtained (ca 24 h). After removal of all the volatiles, LAI(Me)F was extracted with n-hexane (50 mL). Partial removal of the solvent and storage at 0 °C for 2 d afforded colorless crystals of 5. Yield: 0.81 g (85%). Mp: 202 °C. Anal. Calcd for $C_{30}H_{44}AlFN_2$ ($M_r = 478.66$): C, 75.28; H, 9.27; N, 5.85. Found: C, 75.32; H, 9.31; N, 5.83. ¹H NMR (200 MHz, C₆D₆): δ -0.82 (d, 3 H, $J_{H-F} = 2.0$ Hz, AlMe), 1.08 (d, 6 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 1.19 (two overlapped d, 6 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 1.29 (d, 6 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 1.44 (d, 6 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 1.56 (s, 6 H, CMe), 3.16 (sept, 2 H, $J_{H-H} = 6.8$ Hz, $CHMe_2$), 3.64 (sept, 2 H, $J_{H-H} = 6.8$ Hz, $CHMe_2$), 4.98 (s, 1 H, γ -CH), 7.05–7.12 (m, 6 H, Ar). $^{19}\mathrm{F}$ NMR (188 MHz, C₆D₆): δ 8.6 (s, Al-F). MS [EI; m/z (%)]: 478 (10) [M⁺], 463 (100) [M⁺] - Me], 444 (8) [M⁺ - Me - F]. IR (Nujol, cm⁻¹): $\tilde{\nu}$ 1624, 1550, 1531, 1444, 1384, 1318, 1256, 1191, 1177, 1105, 1055, 1023, 941, 879, 806, 797, 757, 720, 663, 629, 448.

Synthesis of LAIF₂ (7). BF₃·OEt₂ (0.43 g, 0.38 mL, 3.0 mmol, 1.34 equiv) was added dropwise to a cooled (-78 °C) solution of LAIH₂ (1.00 g, 2.24 mmol) in toluene (10 mL). The solution was stirred at this temperature for 10 min, slowly warmed to room temperature, and stirred overnight. All volatiles were removed in vacuo, and the residue was crystallized from n-hexane/toluene (1: 1) to give large colorless crystals of $LAIF_2$ (7). Yield: 0.88 g (82%). Mp: 235 °C. Anal. Calcd for $C_{29}H_{41}AlF_2N_2$ ($M_r = 482.63$): C, 72.17; H, 8.56; N, 5.80. Found: C, 72.20; H, 8.58; N, 5.85. ¹H NMR (300 MHz, C_6D_6): δ 1.10 (d, 12 H, $J_{H-H} = 6.9$ Hz, CHMe₂), 1.41 (d, 12 H, $J_{H-H} = 6.9$ Hz, CHMe₂), 1.53 (s, 6 H, CMe), 3.30 (sept, 4 H, $J_{H-H} = 6.9$ Hz, CHMe₂), 4.94 (s, 1 H, γ -CH), 7.03– 7.18 (m, 6 H, Ar). ¹⁹F NMR (188 MHz, C₆D₆): δ 6.8 (s, Al-F). ²⁷Al NMR (78.2 MHz, C₆D₆, TMS): δ 66.9 (s, $w_{1/2} = 1350$ Hz). MS [EI; m/z (%)]: 482 (100) [M⁺], 467 (41) [M⁺ - Me], 447 (18) $[M^+ - MeH - F]$. IR (Nujol, cm⁻¹): $\tilde{\nu}$ 1539, 1318, 1255, 1177, 1102, 1030, 937, 900, 817, 803, 758, 719, 448, 412.

Synthesis of $LGaF_2$ (9). Benzene (60 mL) was added to a mixture of LGaI₂ (1.00 g, 1.35 mmol) and Me₃SnF (0.494 g, 2.70 mmol). The suspension was stirred at room temperature until all the Me₃SnF dissolved to give a clear solution (ca. 4 weeks). After removal of all volatiles under vacuum, the compound was extracted with diethyl ether (30 mL). Partial removal of the ether and keeping the solution at 4 °C afforded colorless crystals. Yield: 0.63 g (90%). Mp: 237 °C. Anal. Calcd for $C_{29}H_{41}F_2GaN_2$ ($M_r = 525.37$): C, 66.30; H, 7.87; F, 7.23; Ga, 13.27; N, 5.33. Found: C, 66.42; H, 7.90; F, 7.19; Ga, 13.10; N, 5.38. ¹H NMR (500 MHz, C_6D_6): δ 1.09 (d, 12 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 1.44 (d, 12 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 1.52 (s, 6 H, CMe), 3.30 (sept, 4 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 4.87 (s, 1 H, γ -CH), 7.05–7.13 (m, 6 H, Ar). ¹⁹F NMR (188 MHz, C_6D_6): δ 38.34 (s, GaF). MS [EI; m/z (%)]: 524 (13) $[M^+]$, 505 (100) $[M^+ - F]$, 486 (33) $[M^+ - 2 F]$. IR (Nujol, cm⁻¹): $\tilde{\nu}$ 1653, 1533, 1349, 1307, 1263, 1177, 1149, 1103, 1056, 1029, 970, 953, 937, 891, 880, 803, 789, 759, 722, 624, 532, 442.

Synthesis of LGa(Me)H (10). LGa(Me)Cl (1.07 g, 2.00 mmol) dissolved in toluene (20 mL) was cooled to -78 °C, and a solution of LiH•BEt₃ in THF (2.0 mL, 2.00 mmol, 1 equiv) was added dropwise. The solution was allowed to warm to room temperature and stirred overnight. After removal of all volatiles the residue was extracted with *n*-hexane (40 mL). Partial removal of the solvent and storage at -26 °C afforded colorless crystals of LGa(Me)H. An additional crop of LGa(Me)H was obtained from the mother liquor. Total yield: 0.72 g (72%). Mp: 177 °C. Anal. Calcd for C₃₀H₄₅GaN₂ ($M_r = 503.41$): C, 71.58; H, 9.01; N, 5.56. Found: C, 71.60; H, 9.03; N, 5.60. ¹H NMR (200 MHz, C₆D₆): δ -0.45 (d, 3 H, $J_{H-H} = 0.8$ Hz, GaMe), 1.16 (two overlapped d, 12 H,

 $J_{\text{H-H}} = 7.2 \text{ Hz}, \text{CH}Me_2$), 1.30 (two overlapped d, 12 H, $J_{\text{H-H}} = 6.8 \text{ Hz}, \text{CH}Me_2$), 1.57 (s, 6 H, CMe), 3.43 (sept, 4 H, $J_{\text{H-H}} = 6.8 \text{ Hz}, \text{CH}Me_2$), 4.81 (s, 1 H, γ -CH), 5.49 (s broad, 1 H, GaH), 7.04–7.13 (m, 6 H, Ar). MS [EI; m/z (%)]: 502 (28) [M⁺], 487 (100) [M⁺ - Me]. IR (Nujol, cm⁻¹): $\tilde{\nu}$ 1825, 1559, 1523, 1495, 1442, 1404, 1388, 1319, 1261, 1232, 1196, 1178, 1104, 1055, 1022, 935, 865, 796, 766, 644, 608, 590, 564, 523, 440.

Synthesis of LGaH₂ (12). LGaI₂ (1.00 g, 1.35 mmol) dissolved in benzene (50 mL) was treated with a solution of LiH·BEt₃ in THF (2.7 mL, 2.7 mmol, 2 equiv). The mixture was stirred at room temperature for 12 h. After removal of all volatiles 12 was extracted with *n*-hexane and the insoluble LiI was filtered off. After the removal of *n*-hexane the compound was dissolved in diethyl ether and colorless crystals were obtained at -27 °C. Yield: 0.70 g (80%). Mp: 135 °C. Anal. Calcd for $C_{29}H_{43}GaN_2$ ($M_r = 489.39$): C, 71.17; H, 8.86; Ga, 14.25; N, 5.72. Found: C, 71.25; H, 8.89; Ga, 14.19, N, 5.73. ¹H NMR (300 MHz, CDCl₃): δ 1.19 (d, 12 H, $J_{\rm H-H} = 6.8$ Hz, CHMe₂), 1.23 (d, 12 H, $J_{\rm H-H} = 6.8$ Hz, CHMe₂), 1.72 (s, 6 H, CMe), 3.20 (sept, 4 H, $J_{H-H} = 6.8$ Hz, CHMe₂), 4.58 (s, broad, 2 H, GaH), 4.85 (s, 1 H, y-CH), 7.10-7.24 (m, 6 H, Ar). MS [EI; m/z (%)]: 488 (65) [M⁺], 487 (100) [M⁺ - H], 486 (8) $[M^+ - 2H]$. IR (KBr, Nujol): $\tilde{\nu}$ 1893, 1861, 1562, 1526, 1405, 1320, 1263, 1253, 1233, 1176, 1101, 1055, 1023, 965, 935, 869, 799, 763, 743, 722, 713, 666, 638, 596, 545, 526, 500, 441.

X-ray Crystal Structure Determination of Complexes 1-5, 7, 9, 10, and 12. Data for the structures were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector and with a mirror-system-monochromated Cu Ka source (for 1-3, 5, 7, and 10) and Stoe IPSD2 system with monochromated Mo K α radiation (for 4, 9, and 12). Intensity measurements were performed on a rapidly cooled crystal. The structures were solved by direct methods (SHELXS-97)59 and refined against all data by full-matrix least squares on F^2 using anisotropic displacement parameters for all non-hydrogen atoms.⁶⁰ The two hydrogen atoms bonded to Ga in 12 were refined with similar distance restraints, while the other hydrogen atoms were included in the refinement at geometrically ideal positions and refined with a riding model except the hydrogen atom bonded to Ga in 10, which was refined freely with U-value fixed to $1.2U_{eq}$ (Ga). In **1** the positions of the methyl group and the chlorine are disordered. The occupancy of the second position refined to 0.11(3). Distance restraints and equal atomic displacement parameters of the two atoms of one position were used for the refinement. The disorder in 10 as mentioned above was not modeled because the occupancy of the second position was too small. The crystal data are summarized in Table 1. Further details are provided in the Supporting Information.

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Supporting Information Available: Detailed X-ray structural data including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and H atom coordinates for 1-5, 7, 9, 10, and 12 (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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