Inorg. Chem. **2006**, *45*, 1853–1860

Inorganic Chemistry
Article

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

Sanjay Singh, Hans-JUrgen Ahn, Andreas Stasch, Vojtech Jancik, Herbert W. Roesky,* Aritra Pal, Mariana Biadene, Regine Herbst-Irmer, Mathias Noltemeyer, and Hans-Georg Schmidt

Institut für Anorganische Chemie der Georg-August-Universität Göttingen, Tammannstrasse 4, D-37077 Göttingen, Germany

Received October 14, 2005

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 $LLi\cdot OEt_2$ with $MeMCl_2$ affords LM(Me)Cl (M = Al (**1**), Ga (**2**), In (**3**)) and $LGaBr_2$ (**4**) with $GaBr_3$. Reduction of LGa(Me)Cl with $LiH\cdot BEt_3$ leads to the formation of LGa(Me)H (**10**). Synthesis of $LGaH_2$ (**12**) has been accomplished by reacting $LGaI_2$ (**8**) with $LiH\cdot BEt_3$. LAl(Me)Cl (**1**) and $LAlH_2$ (**6**) have been converted to LAl(Me)F (**5**) and $LAlF_2$ (**7**), respectively. The former was obtained in a reaction of LAl(Me)Cl with Me_3SnF while the latter was isolated in a reaction of $LAlH_2$ with $BF_3\cdot OEt_2$. Similarly reaction of $LGaI_2$ (**8**) with Me_3SnF affords $LGaF_2$ (**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 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-iPr$_2$C$_6$H$_3$N)}$_2$]. These include the cation $[LAlMe]^+$,[9] the dimethyl derivative $LMMe_2$,[9,10] the dichloride $LMCl_2$, and the diiodide LMI_2 (M = Al, Ga, or In).[16] Synthesis of $LAlMe_2$[10] was reported by Smith et al. whereas other complexes were reported by Power and co-workers.[16] Preparation of $LMCl_2$ was accomplished by the reaction of $LLi\cdot OEt_2$ with MCl_3.[16] Reaction of "GaI" with $LLi\cdot OEt_2$ yields $LGaI_2$ and LGa,[16] whereas $LInI_2$ was prepared by the reaction of $LLi\cdot OEt_2$ with InI_3.[16] $LAlMe_2$[10] and $LGaMe_2$[16] were isolated by the reaction of the corresponding trimethyls with the LH. $LInMe_2$ was prepared by

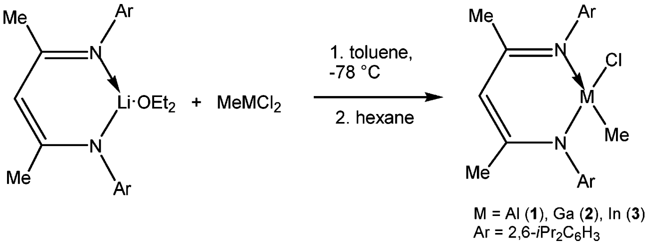
---

* To whom correspondence should be addressed. E-mail: hroesky@gwdg.de.

(1) Bradley, W.; Wright, I. *J. Chem. Soc.* **1956**, 640−648.
(2) Laurence, B.-M.; Lappert, M. F.; Severn, J. R. *Chem. Rev*. **2002**, *102*, 3031−3065 and references therein.
(3) Feldman, J.; McLain, S. J.; Parthasarthy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514−1516.
(4) Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541−4543.
(5) Qian, B.; Scanlon, W. J.; Smith, M. R., III; Motry, D. H. *Organometallics* **1999**, *18*, 1693−1698.
(6) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc*. **1999**, *121*, 7270−7271.
(7) Holland, P. L.; Tolman, W. B. *J. Am. Chem. Soc*. **2000**, *122*, 6331−6332.
(8) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc*. **1998**, *120*, 9384−9385.
(9) Radzewich, C. E.; Guzei, G. T.; Jordan, R. F. *J. Am. Chem. Soc*. **1999**, *121*, 8673−8674.
(10) Qian, B.; Ward, D. L.; Smith, III, M. R. *Organometallics* **1998**, *17*, 3070−3076.
(11) Bailey, P. J.; Dick, C. M. E.; Fabre, S.; Parsons, S. *Dalton Trans*. **2000**, 1655−1661.
(12) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274−4276.
(13) Hardman, N. J.; Eichler, B. E.; Power, P. P. *Chem. Commun*. **2000**, 1991−1992.
(14) Driess, D.; Magull, J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 814−818.
(15) Gibson, V. C.; Maddox, P. J.; Newton, C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun*. **1998**, 1651−1652.
(16) Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P.; Prust, J.; Noltemeyer, M.; Roesky, H. W. *Inorg. Chem.* **2001**, *40*, 2794−2799.

10.1021/ic0517826 CCC: $33.50

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



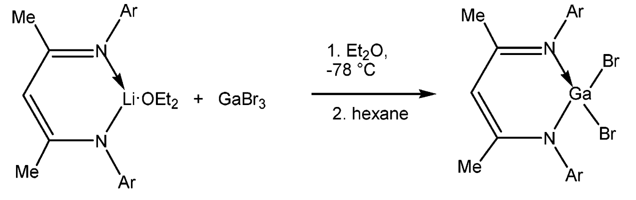
the metathesis of $LInCl_2$ with 2 equiv of MeMgBr.[16] It is noticeable that all these complexes have symmetrical substituents around the metal atom. Presently, there is a growing interest in the chemistry of such complexes where the metal atom has at least two different substituents.

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 synthetically 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 LAl(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 derivatives[23−25] some of which have found applications in ethylene polymerization[23] and polymerization of ϵ-caprolactone.[25] Therefore, it was our primary interest to prepare other derivatives of LAl(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

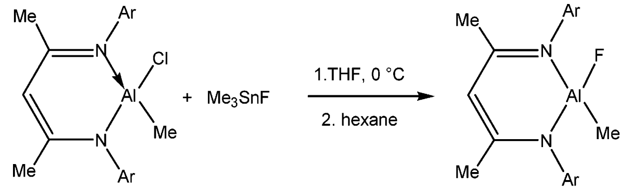
Synthesis of LM(Me)Cl (M = Al **(1)**, Ga **(2)**, In **(3)**) has been accomplished by the reaction of $LLi{\cdot}OEt_2$ with $MeMCl_2$ (Scheme 1). It was observed that the reaction of LH with Me_2MCl leads to a mixture of products which are difficult to separate. Compounds **1**−**3** are examples of novel β-diketiminate metal complexes which are X-ray structurally characterized with metals having two different substituents. Spectroscopic properties of LAl(Me)Cl have already been reported.[26] Compounds LGa(Me)Cl (**2**) and LIn(Me)Cl (**3**) are thermally stable solids with melting points of 190 and 185 °C, respectively, and are sensitive to moisture. ^{1}H 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. $LGaBr_2$ (**4**) was synthesized by the reaction of $LLi{\cdot}OEt_2$ with $GaBr_3$ in diethyl ether (Scheme 2). $LGaBr_2$ (**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.

Scheme 2. Preparation of β-Diketiminate Gallium Dibromide



4

Scheme 3. Preparation of the β-Diketiminate Methylaluminum Fluoride



1

Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

5

Trimethyltin fluoride has proved to be a versatile fluorinating agent particularly in the conversion of groups 4−6 and 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 Me_3SnF in THF results in the complete conversion of **1** to LAl(Me)F (**5**) (Scheme 3) which was characterized by its ^{19}F 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 $LAlF_2$ (**7**) was isolated (Scheme 4). A singlet in the ^{19}F 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

---

(17) Bai, G.; Peng, Y.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1132−1135.

(18) Bai, G.; Roesky, H. W.; Li, J.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5502−5506.

(19) Jancik, V.; Pineda, L. W.; Pinkas, J.; Roesky, H. W.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2142−2145.

(20) Jancik, V.; Pineda, L. W.; Stückl, A. C.; Roesky, H. W.; Herbst-Irmer, R. *Organometallics* **2005**, *24*, 1511−1515.

(21) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1419−1421.

(22) Roesky, H. W.; Singh, S.; Jancik, V.; Chandrasekhar, V. *Acc. Chem. Res.* **2004**, *37*, 969−981.

(23) Bai, G.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2005**, *127*, 3449−3455.

(24) Singh, S.; Kumar, S. S.; Chandrasekhar, V.; Ahn, H.-J.; Biadene, M.; Roesky, H. W.; Hosmane, N. S.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem., Int. Ed.* **2004**, *43*, 4940−4943.

(25) Chai, J. F.; Jancik, V.; Singh, S.; Zhu, H.; He, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hosmane, N. S. *J. Am. Chem. Soc.* **2005**, *127*, 7521−7528.

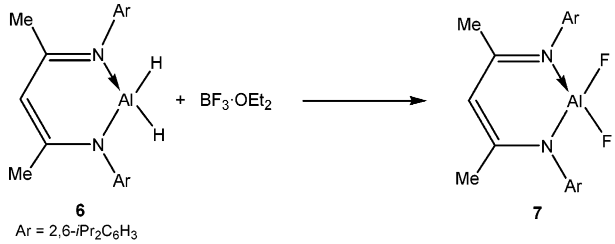
(26) Zhu, H.; Chai, J. F.; He, C.; Bai, G.; Roesky, H. W.; Jancik, V.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, *24*, 380−384.

(27) Pinkas, J.; Roesky, H. W. *J. Fluorine Chem.* **2003**, *122*, 125−150.

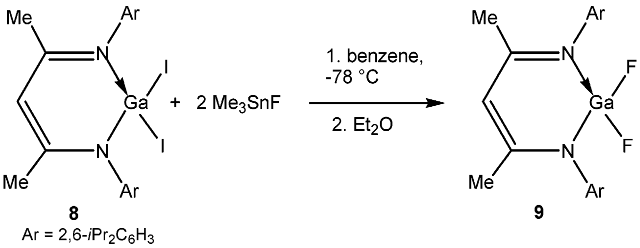
(28) Roesky, H. W.; Keller, K. *J. Fluorine Chem.* **1999**, *100*, 217−226.

(29) Hohmeister, H.; Wessel, H.; Lobinger, P.; Roesky, H. W.; Müller, P.; Usón, I.; Schmidt, H.-G.; Noltemeyer, M.; Magull, J. *J. Fluorine Chem.* **2003**, *120*, 59−64.

Scheme 4. Preparation of the *β*-Diketiminate Aluminum Difluoride



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

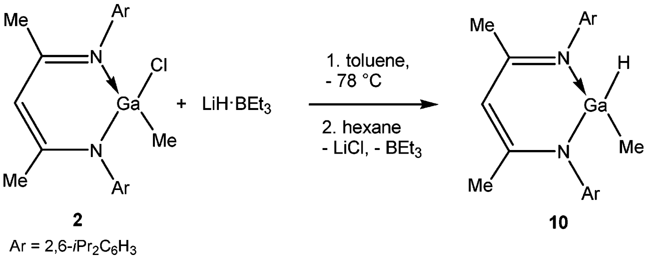


compound $LGaF_2$ (**9**) was synthesized by the reaction of $LGaI_2$ **(8)** with Me_3SnF (Scheme 5). ^{19}F NMR of **9** exhibits the Ga−*F* to resonate at *δ* 38.3 ppm. The mass spectrum of **9** reveals the base peak as $[M^+ - F]$ at *m/z* 505 and the molecular ion at *m/z* 523 $[M^+]$ in low intensity.

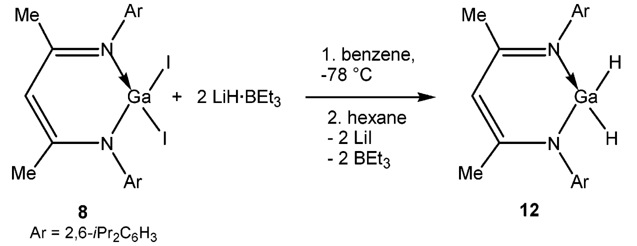
A number of hydrides of aluminum have been prepared ranging from mono-,[30,33] di-,[30−34] and trihydrides.[35−38] The latter has been a very strong and useful reducing agent in the form of alane and aluminates. The corresponding gallium compounds[33,38,39] are also known but their stability is lower 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, $GaH_3 \cdot NMe_3$ 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 $LiH \cdot BEt_3$ in toluene smoothly affords LGa(Me)H **(10)** in good yield (Scheme 6).

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



Scheme 7. Preparation of *β*-Diketiminate-Supported Gallium Dihydride



On the contrary reaction of $LiH \cdot BEt_3$ 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 $MeAlH_2 \cdot NMe_3$[43] or reduction of LAl(Me)Cl (**1**) with $LiAlH_4$ 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 $LGaH_2$ (**12**) involves the conversion of $LGaI_2$ **(8)** to $LGaH_2$ with $LiH \cdot BEt_3$ (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

---

(30) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 3262−3267.
(31) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 5611−5612.
(32) Wehmschulte, R. J.; Grigsby, W. J.; Schiemenz, B.; Bartlett, R. A.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 6694−6702.
(33) Isom, H. S.; Cowley, A. H.; Decken, A.; Sissingh, F.; Corbelin, S.; Lagow, R. J. *Organometallics* **1995**, *14*, 2400−2406.
(34) Contreras, L.; Cowley, A. H.; Gabbaï, F. P.; Jones, R. A.; Carrano, C. J.; Bond, M. R. *J. Organomet. Chem.* **1995**, *489*, C1−C3.
(35) Downs, A. J.; Pulham, C. R.; *Chem. Soc. Rev*. **1994**, *23*, 175−184.
(36) Ruff, J. K. *Inorg. Synth.* **1967**, *9*, 30−37.
(37) Twamley, B.; Hardman, N. J.; Power, P. P. *Acta Crystallogr.* **2001**, *E57*, m227−m228.
(38) Pulham, C. R.; Downs, A. J.; Goode, M. J.; Rankin, D. W. H.; Robertson, H. E. *J. Am. Chem. Soc.* **1991**, *113*, 5149−5162.
(39) Cowley, A. H.; Gabbaï, F. P.; Atwood, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 1559−1560.
(40) Wehmschulte, R. J.; Ellison, J. J.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 6300−6303.
(41) Storr, A.; Wiebe, V. G. *Can. J. Chem.* **1969**, *47*, 673−679.
(42) Cowley, A. H.; Gabbaï, F. P.; Isom, H. S.; Decken, A. *J. Organomet. Chem.* **1995**, *500*, 81−88.
(43) Peters, F. M.; Bartocha, B.; Bilbo, A. J. *Can. J. Chem.* **1963**, *41*, 1051−1058.

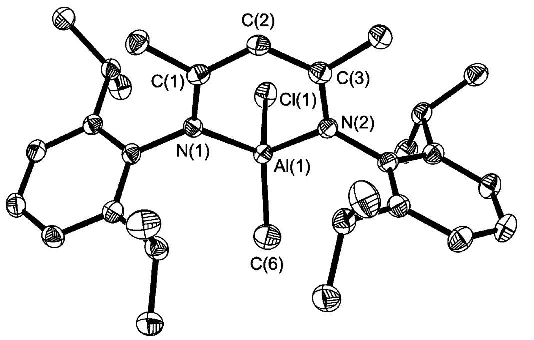


Figure 1. Molecular structure of LAl(Me)Cl (**1**) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

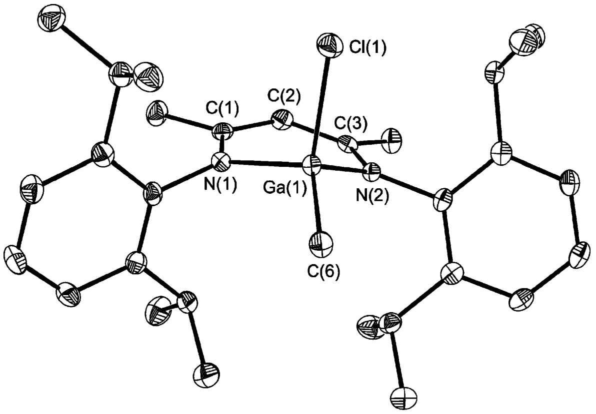


Figure 2. Molecular structure of LGa(Me)Cl (**2**) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

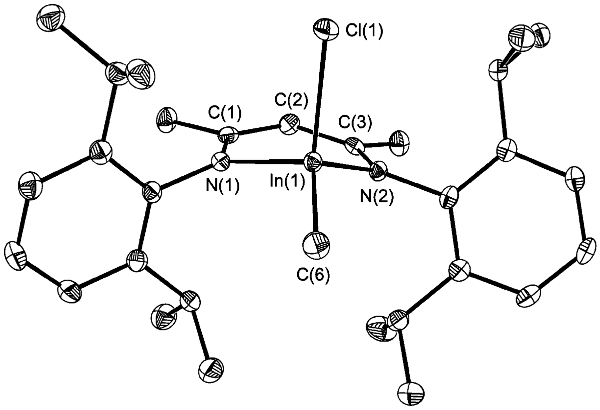


Figure 3. Molecular structure of LIn(Me)Cl (**3**) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

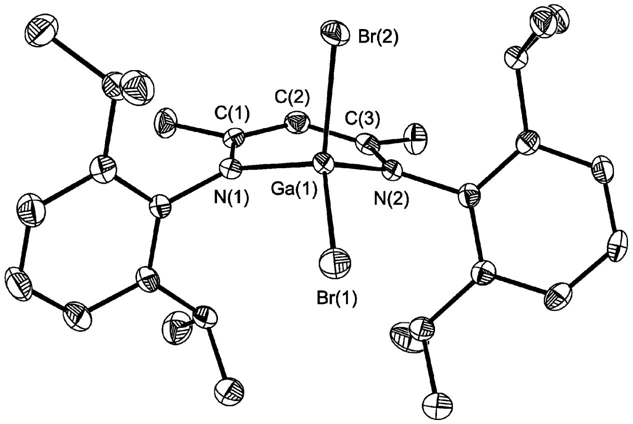


Figure 4. Molecular structure of $LGaBr_2$ (**4**) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

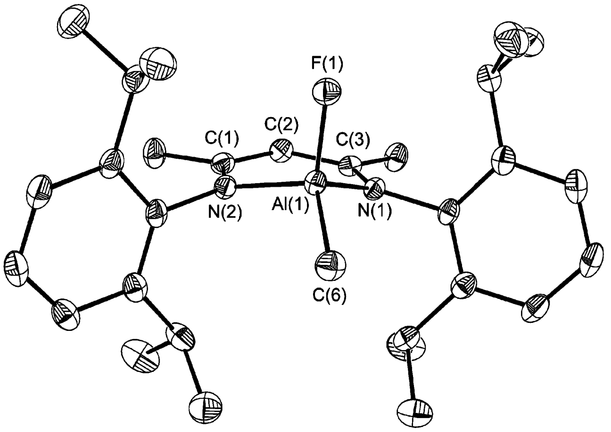


Figure 5. Molecular structure of LAl(Me)F (**5**) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

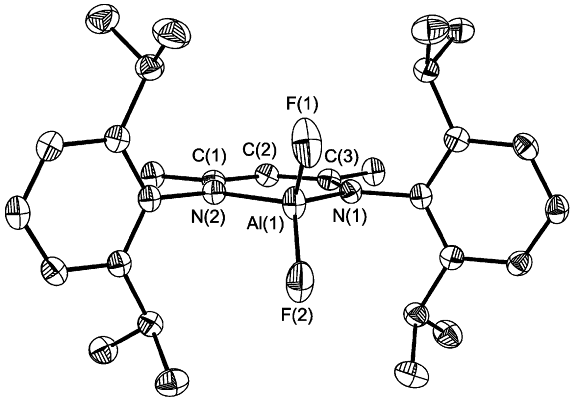


Figure 6. Molecular structure of $LAlF_2$ (**7**) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

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 C_3N_2M ring is planar or nearly planar (observed in LAl,[12] $LAlH_2$,[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 C_2N_2 plane, but the deviation is not so large as in the case of the metal center. This boat 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 $LGaF_2$ (**9**) at 100.8(1)°, depending on the covalent radii

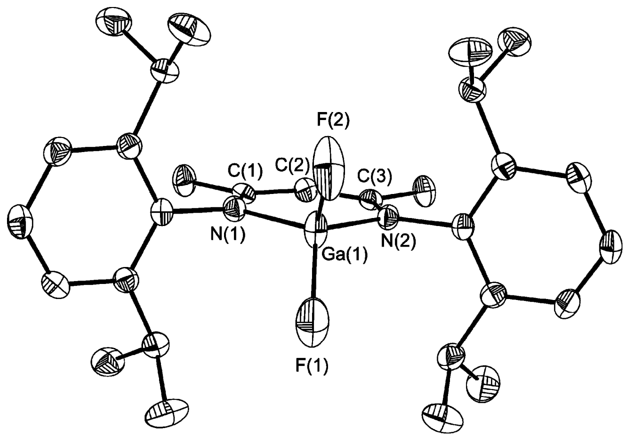


Figure 7. Molecular structure of $LGaF_2$ (**9**) with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity.

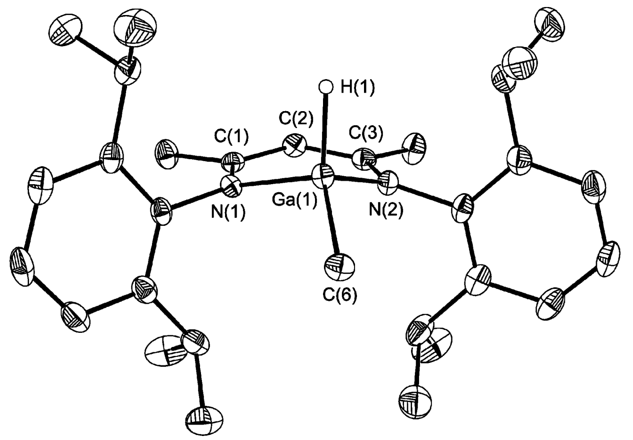


Figure 8. Molecular structure of LGa(Me)H (**10**) with 50% thermal ellipsoids. All hydrogen atoms except that on Ga(1) are omitted for clarity.

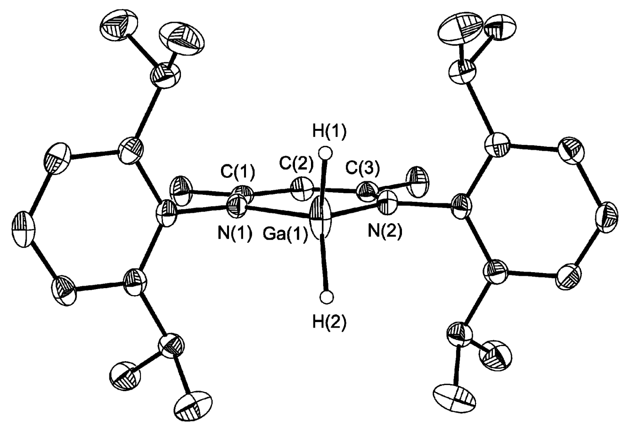


Figure 9. Molecular structure of $LGaH_2$ (**12**) with 50% thermal ellipsoids. All hydrogen atoms except those on Ga(1) are omitted for clarity.

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 Refinement for Complexes **1**−**5**, **7**, **10**, and **12**

param	**1**	**2**	**3**	**4**	**5**	**7**	**9**	**10**	**12**
formula	$C_{30}H_{44}AlClN_2$	$C_{30}H_{44}ClGaN_2$	$C_{30}H_{44}ClInN_2$	$C_{29}H_{41}Br_2GaN_2$	$C_{30}H_{44}AlFN_2$	$C_{29}H_{41}AlF_2N_2$	$C_{29}H_{41}F_2GaN_2$	$C_{30}H_{45}GaN_2$	$C_{29}H_{43}GaN_2$
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)
λ, Å	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, Å	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
ρ_{calcd}, g/cm^3	1.141	1.240	1.308	1.453	1.114	1.179	1.272	1.167	1.179
μ, 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 × 0.20 × 0.10	0.10 × 0.10 × 0.07	0.10 × 0.10 × 0.05	0.30 × 0.30 × 0.20	0.20 × 0.10 × 0.10	0.60 × 0.50 × 0.50	0.20 × 0.20 × 0.20	0.30 × 0.30 × 0.20	0.30 × 0.30 × 0.20
θ range for data collcn, 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 collcd	23769	16011	15305	16490	11809	24658	40901	17143	38900
no. of indent reflcns (R_{int})	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
R1,[a] wR2[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] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

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 LAlCl$_2$ (2.134(1) and 2.119(1) Å, average 2.126 Å).[16] The C(6)−Al(1)−Cl(1) angle 114.9(4)° lies between the angles of C(1)−Al(1)−C(2) 115.4(2)° in LAlMe$_2$[10] and Cl(1)−Al(1)−Cl(2) 108.0(1)° in LAlCl$_2$ (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 LGaMe$_2$ (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 LGaCl$_2$ (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)° in LGaMe$_2$[16] and Cl(1)−Ga(1)−Cl(2) at 110.20(4)° in LGaCl$_2$.[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 LInCl$_2$ (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 LInCl$_2$[16] but narrower than the C(30)−In(1)−C(31) 130.94(6)° in LInMe$_2$.[16]

The molecular structure of LGaBr$_2$ (**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 [PyGaBr$_2$]$_2$ (2.350(2) Å)[45] and *t*Bu$_3$SiGaBr$_2$·THF (2.360(1) Å)[46] and [(3,5-Me$_2$C$_6$H$_3$CH$_2$)$_2$GaBr$_2$]$_2$ (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 [PyGaBr$_2$]$_2$ (105.8(1)°)[45] and *t*Bu$_3$SiGaBr$_2$·THF (105.6(1)°)[46] and [(3,5-Me$_2$C$_6$H$_3$CH$_2$)$_2$GaBr$_2$]$_2$ (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)°).

The Al(1)−C(6) bond distance in LAl(Me)F (**5**) (1.944(2) Å) is slightly shorter than that found in LAlMe$_2$ (average 1.964 Å).[10] The Al−F bond length (1.679(1) Å) is slightly longer than that observed in LAlF$_2$ (**7**) (1.656(1) and 1.650(1) Å) and identical in [OCMeCHCMeN(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$AlF (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$_3$Si)$_3$CAlF$_2$}$_3$] (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)°, which is wider than the F(1)−Al(1)−F(2) angle of 107.8(1)° in **7**, probably due to the smaller size of the F atom compared to that of the Me group. Ga−F distances observed in LGaF$_2$ (**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] [Mes$_2$Ga(F)(*t*BuNH$_2$)] (1.838(3) Å)[51] [{(Me$_3$Si)$_2$HC}$_2$GaF]$_2$ (average 1.966 Å),[52] and [Mes$_2$GaF]$_2$ (1.947(2) 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

---

(44) For covalent atomic radii, see the Web page of the Cambridge Structural Database: http://www.ccdc.cam.ac.uk/products/csd/radii/.

(45) Small, R. W. H.; Worrall, I. J. *Acta Crystallogr.* **1982**, *B38*, 86−87.

(46) Wiberg, N.; Blank, T.; Westerhausen, M.; Schneiderbauer, S.; Schnöckel, H.; Krossing, I.; Schnepf, A. *Eur. J. Inorg. Chem.* **2002**, 351−356.

(47) Kopp, M. R.; Neumüller, B. *Z. Naturforsch.* **1998**, *53B*, 545−551.

(48) Yu, R.-C.; Hung, C.-H.; Huang, J.-H.; Lee, H.-Y.; Chen, J.-T. *Inorg. Chem.* **2002**, *41*, 6450−645.

(49) Schnitter, C.; Klimek, K.; Roesky, H. W.; Albers, T.; Schmidt, H.-G.; Röpken, C.; Parisini, E. *Organometallics* **1998**, *17*, 2249−2257.

(50) Wynne, K. J. *Inorg. Chem.* **1985**, *24*, 1339−1343.

(51) Kräuter, T.; Neumüller, B. *Z. Anorg. Allg. Chem.* **1995**, *621*, 597−606.

in $[\{(Me_3Si)_2HC\}_2GaF]_2$[52] but wider than that observed in $[Mes_2GaF]_2$ (78.9(1)°).[53] The N(1)−Ga(1)−N(2) angle within the C_3N_2Ga 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 $LGaBr_2$ (**4**) (99.8(1)°).

The structures of the complexes LGa(Me)H (**10**) and $LGaH_2$ (**12**) are analogous to their parent compounds LGa(Me)Cl (**2**) and $LGaI_2$, 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 $[(t\mathrm{BuO})_2GaH)]_2$ (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 Me_3SnF or $BF_3{\cdot}OEt_2$ 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 Al[23] and Ga[20] 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. $MeGaCl_2$,[55] $MeInCl_2$,[56] LH,[3] $LLi{\cdot}OEt_2$,[57] $LGaCl_2$,[16] $LGaI_2$,[16] $MeAlH_2{\cdot}NMe_3$,[43] and Me_3SnF[58] were prepared as described in the literature. $MeAlCl_2$, $BF_3{\cdot}OEt_2$, and $LiH{\cdot}BEt_3$ were purchased from Aldrich and were used without purification.

Physical Measurements. The ^1H NMR spectra were recorded on Bruker AM 200 NMR spectrometer with $SiMe_4$ as external standard, and ^{19}F 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). $LLi{\cdot}OEt_2$ (1.49 g, 3.00 mmol) dissolved in toluene (30 mL) was cooled to −78 °C, and $MeGaCl_2$ (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 (C_6D_6, 200 MHz): δ −0.31 (s, 3 H, Ga*Me*), 1.04 (d, 6 H, J_{H-H} = 6.8 Hz, CH*Me*$_2$), 1.19 (two overlapped d, 12 H, J_{H-H} = 6.8 Hz, CH*Me*$_2$), 1.48 (d, 6 H, J_{H-H} = 6.8 Hz, CH*Me*$_2$), 1.57 (s, 6 H, C*Me*), 3.15 (sept, 2 H, J_{H-H} = 6.8 Hz, C*H*Me$_2$), 3.87 (sept, 2 H, J_{H-H} = 6.8 Hz, C*H*Me$_2$), 4.90 (s, 1 H, *γ*-C*H*), 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 $LLi{\cdot}OEt_2$ and 0.40 g (2.00 mmol) for $MeInCl_2$. Yield: 0.75 g (65%). Mp: 185 °C. Anal. Calcd for $C_{30}H_{44}ClInN_2$ (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 (C_6D_6, 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*$_2$), 1.58 (s, 6 H, C*Me*), 3.15 (sept, 2 H, J_{H-H} = 6.8 Hz, C*H*Me$_2$), 3.83 (sept, 2 H, J_{H-H} = 6.8 Hz, C*H*Me$_2$), 4.80 (s, 1 H, *γ*-C*H*), 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 $LGaBr_2$ (4). $GaBr_3$ (1.00 g, 3.23 mmol) dissolved in diethyl ether (40 mL) was cooled to −78 °C, and a solution of $LLi{\cdot}Et_2O$ (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, $CDCl_3$): δ 1.20 (d, 12 H, J_{H-H} = 6.8 Hz, CH*Me*$_2$), 1.31 (d, 12 H, J_{H-H} = 6.8 Hz, CH*Me*$_2$), 1.90 (s, 6 H, C*Me*), 3.37 (sept, 4 H, J_{H-H} = 6.8 Hz, C*H*Me$_2$), 5.31 (s, 1 H, *γ*-C*H*), 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 LAl(Me)F (5). THF (40 mL) was added to a mixture of LAl(Me)Cl (0.99 g, 2.00 mmol) and Me_3SnF (0.37 g,

---

(52) Uhl, W.; Graupner, R.; Hahn, I.; Spies, T.; Frank, W. *Eur. J. Inorg. Chem.* **1998**, 355−360.

(53) Neumüller, B.; Gahlmann, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1701−1702.

(54) Veith, M.; Faber, S.; Wolfgang, H.; Huch, V. *Chem. Ber.* **1996**, *129*, 381−384.

(55) Beachley, O. T., Jr.; Rosenblum, D. B.; Macrae, D. J. *Organometallics* **2001**, *20*, 945−949.

(56) $MeInCl_2$ was prepared in a reaction of Me_3In and $InCl_3$ in 1:2 stoichiometric ratio by using the procedure similar to that reported for $MeGaCl_2$.[55]

(57) Stender, M.; Wright, R. J.; Eichler, B. E.; Prust, J.; Olmstead, M. M.; Roesky, H. W.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **2001**, 3465−3469.

(58) Roesky, H. W.; Keller, K. *J. Fluorine Chem.* **1998**, *89*, 3−4.

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, LAl(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. ^{1}H NMR (200 MHz, C_6D_6): δ −0.82 (d, 3 H, $J_{H-F} = 2.0$ Hz, Al*Me*), 1.08 (d, 6 H, $J_{H-H} = 6.8$ Hz, CH*Me*$_2$), 1.19 (two overlapped d, 6 H, $J_{H-H} = 6.8$ Hz, CH*Me*$_2$), 1.29 (d, 6 H, $J_{H-H} = 6.8$ Hz, CH*Me*$_2$), 1.44 (d, 6 H, $J_{H-H} = 6.8$ Hz, CH*Me*$_2$), 1.56 (s, 6 H, C*Me*), 3.16 (sept, 2 H, $J_{H-H} = 6.8$ Hz, C*H*Me$_2$), 3.64 (sept, 2 H, $J_{H-H} = 6.8$ Hz, C*H*Me$_2$), 4.98 (s, 1 H, γ-C*H*), 7.05−7.12 (m, 6 H, *Ar*). ^{19}F NMR (188 MHz, C_6D_6): 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 LAlF$_2$ (7). $BF_3 \cdot OEt_2$ (0.43 g, 0.38 mL, 3.0 mmol, 1.34 equiv) was added dropwise to a cooled (−78 °C) solution of LAlH$_2$ (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 LAlF$_2$ (**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. ^{1}H NMR (300 MHz, C_6D_6): δ 1.10 (d, 12 H, $J_{H-H} = 6.9$ Hz, CH*Me*$_2$), 1.41 (d, 12 H, $J_{H-H} = 6.9$ Hz, CH*Me*$_2$), 1.53 (s, 6 H, C*Me*), 3.30 (sept, 4 H, $J_{H-H} = 6.9$ Hz, C*H*Me$_2$), 4.94 (s, 1 H, γ-C*H*), 7.03−7.18 (m, 6 H, *Ar*). ^{19}F NMR (188 MHz, C_6D_6): δ 6.8 (s, Al−*F*). ^{27}Al NMR (78.2 MHz, C_6D_6, 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 LGaI$_2$ (1.00 g, 1.35 mmol) and Me$_3$SnF (0.494 g, 2.70 mmol). The suspension was stirred at room temperature until all the Me$_3$SnF 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. ^{1}H NMR (500 MHz, C_6D_6): δ 1.09 (d, 12 H, $J_{H-H} = 6.8$ Hz, CH*Me*$_2$), 1.44 (d, 12 H, $J_{H-H} = 6.8$ Hz, CH*Me*$_2$), 1.52 (s, 6 H, C*Me*), 3.30 (sept, 4 H, $J_{H-H} = 6.8$ Hz, C*H*Me$_2$), 4.87 (s, 1 H, γ-C*H*), 7.05−7.13 (m, 6 H, *Ar*). ^{19}F NMR (188 MHz, C_6D_6): δ 38.34 (s, Ga*F*). 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 $LiH \cdot BEt_3$ 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 $C_{30}H_{45}GaN_2$ ($M_r = 503.41$): C, 71.58; H, 9.01; N, 5.56. Found: C, 71.60; H, 9.03; N, 5.60. ^{1}H NMR (200 MHz, C_6D_6): δ −0.45 (d, 3 H, $J_{H-H} = 0.8$ Hz, Ga*Me*), 1.16 (two overlapped d, 12 H, $J_{H-H} = 7.2$ Hz, CH*Me*$_2$), 1.30 (two overlapped d, 12 H, $J_{H-H} = 6.8$ Hz, CH*Me*$_2$), 1.57 (s, 6 H, C*Me*), 3.43 (sept, 4 H, $J_{H-H} = 6.8$ Hz, C*H*Me$_2$), 4.81 (s, 1 H, γ-C*H*), 5.49 (s broad, 1 H, Ga*H*), 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 LGaH$_2$ (12). LGaI$_2$ (1.00 g, 1.35 mmol) dissolved in benzene (50 mL) was treated with a solution of $LiH \cdot BEt_3$ 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. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.19 (d, 12 H, $J_{H-H} = 6.8$ Hz, CH*Me*$_2$), 1.23 (d, 12 H, $J_{H-H} = 6.8$ Hz, CH*Me*$_2$), 1.72 (s, 6 H, C*Me*), 3.20 (sept, 4 H, $J_{H-H} = 6.8$ Hz, C*H*Me$_2$), 4.58 (s, broad, 2 H, Ga*H*), 4.85 (s, 1 H, γ-C*H*), 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 Kα source (for **1**−**3**, **5**, **7**, and **10**) and Stoe IPSD2 system with monochromated Mo Kα 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.

Acknowledgment. This work was supported by the Göttinger Akademie der Wissenschaften. S.S. thanks the Graduiertenkolleg (GRK 782) Spektroskopie und Dynamik molekularer Aggregate, Ketten und Knäuel for a graduate student fellowship.

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.

IC0517826

---

(59) Sheldrick, G. M. SHELXS-97, Program for Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(60) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.