Lithium, Aluminum, and Gallium Complexes of the C_6F_5-Substituted β-Diketiminate Ligand $[HC(CMe)_2(NC_6F_5)_2]^-$

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Dedicated to Professor Herbert W. Roesky on the Occasion of his 70th Birthday

Abstract. The β-aminoimine $[HC(CMe)_2(NC_6F_5)_2]H$ (**1**) is readily converted into the lithium β-diketiminate $[HC(CMe)_2(NC_6F_5)_2]Li{\cdot}OEt_2$ (**2**) by treatment with MeLi. The aluminum and gallium derivatives $[\{HC(CMe)_2(NC_6F_5)_2\}MMe_2]$ (M = Al (**3**); Ga (**4**)) have been prepared via the CH_4 elimination reactions of **1** with MMe_3. The X-ray crystal structures of **1** − **4** have been determined and the trends in metrical parameters are discussed.

Keywords: β-Diketiminates; Lithium; Aluminum; Gallium; Crystal structure

Introduction

β-Diketiminates continue to attract considerable interest as supporting ligands due to their range of coordination modes and their propensity to stabilize low oxidation states [1]. Illustrative of the latter point is the isolation and characterization of novel aluminum(I) and gallium(I) β-diketiminates by *Roesky* et al. [2] and *Power* et al. [3], respectively. In the context of main group chemistry, the β-diketiminate ligands that have been employed thus far typically feature alkyl and/or aryl substituents [1]. Considerably less information is available regarding β-diketiminate ligands bearing electron-withdrawing groups. However, one such ligand, $[HC(CMe)_2(NC_6F_5)_2]^-$, has been reported [4]. At the present time, this ligand has only been used for the synthesis of two iron complexes [4]. To the best of our knowledge, there is no record of the use of this ligand in main group chemistry. However, we have recently employed the $[HC(CMe)_2(NC_6F_5)_2]^-$ ligand for the isolation of an oxoborane (LB=O) stabilized by complexation to aluminum trichloride [5]. In the present paper, we describe the syntheses and X-ray crystal structures of lithium, aluminum, and gallium complexes supported by the $[HC(CMe)_2(NC_6F_5)_2]^-$ ligand. We also report the structure of the corresponding β-aminoimine, $[HC(CMe)_2(NC_6F_5)_2]H$.

Results and Discussion

Syntheses

The lithium derivative $[HC(CMe)_2(NC_6F_5)_2]Li{\cdot}OEt_2$ (**2**), a potentially valuable synthon, is readily prepared in high yield by treatment of $[HC(CMe)_2(NC_6F_5)_2]H$ (**1**) with MeLi in hexane/diethyl ether solution. The compound crystallizes with a molecule of Et_2O. The fact that the N-H ^1H NMR chemical shift of $[HC(CMe)_2(NC_6F_5)_2]H$ is close to δ 12 [4] implies that this proton should be sufficiently acidic to render protonolysis a viable synthetic route to β-diketiminate complexes. Indeed, *Power* et al. [4] have employed **1** for the protonolysis of metal amides in order to prepare the iron β-diketiminates referred to earlier. We therefore adopted the methane elimination approach outlined below for the synthesis of the aluminum and gallium dimethyl derivatives, **3** and **4**.

$$[HC(CMe)_2(NC_6F_5)_2]H + MMe_3 \xrightarrow[-CH_4]{} [\{HC(CMe)_2(NC_6F_5)_2\}MMe_2]$$

M = Al(**3**), Ga(**4**)

X-ray Crystal Structures

To the best of our knowledge, **1** is only the third structurally characterized β-aminoimine, the other two being H(Ph)NC(Me)CHC(Me)N(Ph) (**5**) [6] and H(Ar)NC(Me)CH(Me)N(Ar) (Ar = 2,6-*i*-$Pr_2C_6H_3$) (**6**) [7]. Overall, the structure of **1** (Figure 1 and Table 1) is very similar to those of **5** and **6**. The fact that the N(2)-C(4) bond distance in **1** (1.300(3) Å) is shorter than those in **5** (1.314(8) Å) and **6** (1.313(4) Å) might suggest that there is slightly more double bond localization in the case of **1**. However, note that the C(2)-C(3) bond distance in **1** (1.358(3) Å) is the same as those in **5** (1.352(8) Å) and **6** (1.362(4) Å) within experimental error. A distinctive feature of the structure of **5** is that the nitrogen hydrogen atom is located equidistantly between the two nitrogen atoms. However, for **1** and **6** this hydrogen atom is much closer to one nitrogen (N(1) in Fig. 1) than the other. This aspect has already been commented on in the context of the structures of **5** and **6** [7].

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Table 1 Selected bond distances/Å and angles/deg for **1** − **4**.

1		**2**		**3**		**4**	
N(1)-C(2)	1.361(3)	N(1)-Li	1.925(5)	N(1)-Al	1.926(2)	N(1)-Ga	1.987(3)
N(1)-C(6)	1.400(3)	N(1)-C(2)	1.336(3)	N(1)-C(2)	1.333(3)	N(1)-C(2)	1.334(5)
C(2)-C(3)	1.358(3)	C(2)-C(3)	1.398(4)	C(2)-C(3)	1.395(3)	C(2)-C(3)	1.381(6)
C(3)-C(4)	1.438(3)	C(3)-C(4)	1.405(3)	C(3)-C(4)	1.395(3)	C(3)-C(4)	1.411(6)
N(2)-C(4)	1.300(3)	N(2)-C(4)	1.330(3)	N(2)-C(4)	1.343(3)	N(2)-C(4)	1.330(5)
N(2)-C(12)	1.406(2)	N(2)-Li	1.925(5)	N(2)-Al	1.917(2)	N(2)-Ga	2.007(3)
C(2)-N(1)-C(6)	126.87(17)	Li-O	1.896(4)	C(18)-Al	1.957(3)	C(18)-Ga	1.956(5)
N(1)-C(2)-C(3)	120.35(17)	N(1)-Li-N(2)	97.4(2)	C(19)-Al	1.947(3)	C(19)-Ga	1.967(5)
C(2)-C(3)-C(4)	125.79(18)	Li-N(1)-C(2)	123.5(2)	N(1)-Al-N(2)	93.99(8)	N(1)-Ga-N(2)	92.5(1)
C(3)-C(4)-N(2)	119.45(17)	N(1)-C(2)-C(3)	122.6(2)	Al-N(1)-C(4)	126.8(2)	Ga-N(1)-C(2)	126.1(3)
C(4)-N(2)-C(12)	122.18(17)	C(2)-C(3)-C(4)	130.0(2)	N(1)-C(4)-C(3)	122.2(2)	N(1)-C(2)-C(3)	123.1(3)
		C(3)-C(4)-N(2)	122.2(2)	C(4)-C(3)-C(2)	128.1(2)	C(2)-C(3)-C(4)	129.8(4)
		C(4)-N(2)-Li	124.0(2)	C(3)-C(2)-N(2)	122.6(2)	C(3)-C(4)-N(2)	122.3(4)
				C(2)-N(2)-Al	126.2(1)	C(4)-N(2)-Ga	126.0(3)
				C(18)-Al-C(19)	118.9(1)	C(18)-Ga-C(19)	123.9(2)

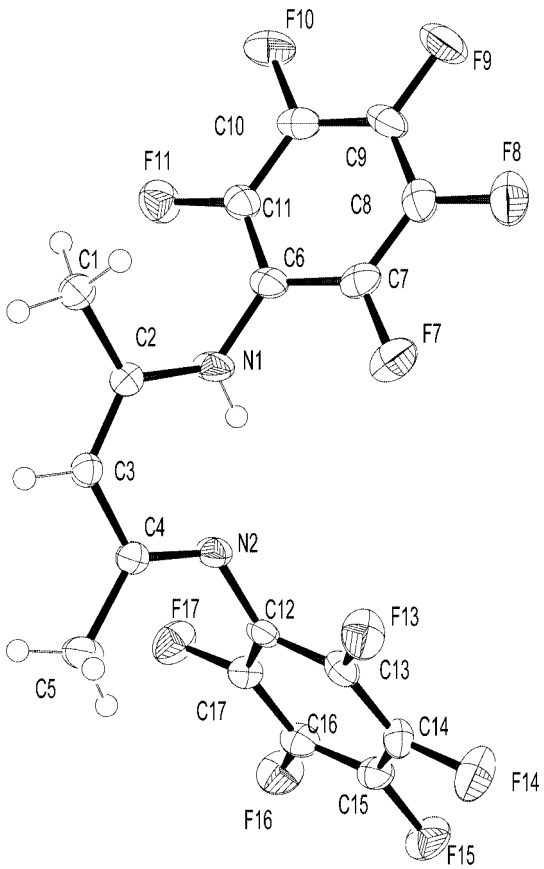

Fig. 1 Molecular structure of $[HC(CMe)_2(NC_6F_5)_2]H$ (**1**) showing the atom numbering scheme.Thermal ellipsoids are set to 30 % probability.

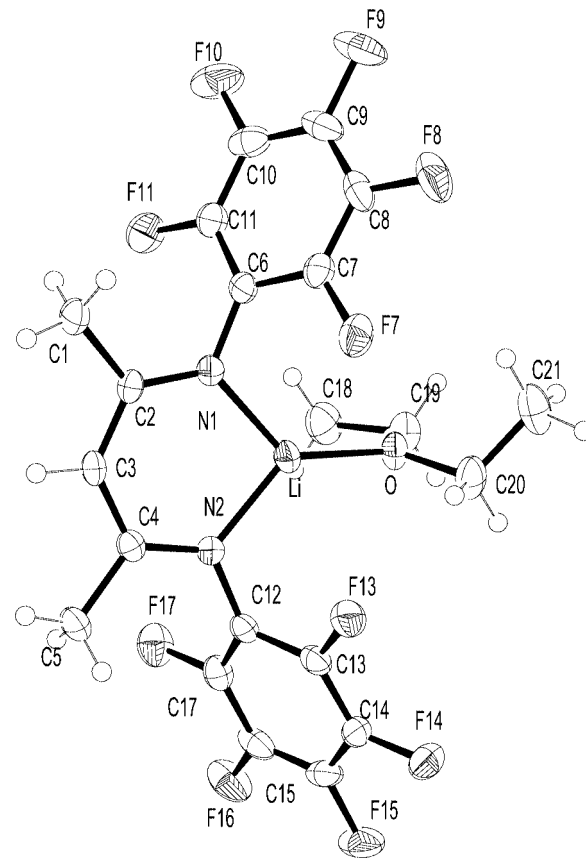

Fig. 2 Molecular structure of $[HC(CMe)_2(NC_6F_5)_2]Li{\cdot}OEt_2$ (**2**) showing the atom numbering scheme.Thermal ellipsoids are set to 30 % probability.

The replacement of the nitrogen hydrogen atom of **1** by a $Li{\cdot}OEt_2$ moiety results in **2** which, possesses a much more symmetrical structure that is indicative of π-bonding in the C_3N_2 fragment (Fig. 2 and Table 1). Thus, the two N-C and the two C-C bond distances are the same within experimental error and the sum of bond angles within the C_3N_2Li ring is 719.7(2)°. The Li atom, which is displaced from the extended C_3N_2 plane by 0.018 Å, possesses a distorted trigonal planar geometry (sum of bond angles at Li = 359.7(3)°). The average N-C and C-C bond distances in **2** (1.333(3) and 1.401(4) Å, respectively) are very similar to those reported for the lithium monoetherate, $[Dipp_2nacnacLi(OEt_2)]$ (**7**) (1.324(3) and 1.402(3) Å, respectively; $Dipp_2$ = C_6H_3-2,6-Pr^i_2) [7]. Likewise, the Li-N and Li-O bond dis-

tances in **2** (1.925(5) and 1.896(4) Å, respectively) are very similar to those reported for **7** [7] (1.915(4) (av.) and 1.911(4) Å, respectively). The structure of **7** has also been reported by *Tolman* et al. [8].

Previously reported, structurally characterized (β-diketiminate)$AlMe_2$ compounds include [($Dipp_2$nacnac)$AlMe_2$] (**8**) [9, 10] ($Dipp_2$ = 2,6-*i*-$Pr_2C_6H_3$ and [{HC(CMe)$_2$-(N-*p*-tolyl)$_2$}$AlMe_2$] (**9**) [10]. A characteristic feature of both compounds is the pronounced puckering of the C_3N_2Al ring. This puckering can be expressed as the distance of the metal atom from the averaged extended C_3N_2 plane or as the dihedral angle between the C_3N_2 and N_2metal planes. For **8** and **9**, the displacement of the Al atom from the β-diketiminate plane amounts to 0.72 and 0.33 Å, respectively. In the case of **3** (Fig. 3 and Table 1), this displacement is considerably less (0.073 Å) hence the C_3N_2Al ring is close to planarity. The ring puckering has been attributed to steric interactions between bulky groups such as Dipp and the metal substituents [11]. Moreover, a correlation has been observed between the N-Al-N angle and the extent of ring puckering in the sense that the more acute this angle, the greater the extent of ring puckering [11]. In this context, it is interesting to note that the N-Al-N angle in **3** (93.99(8)°) is more acute than those in **8** (96.18(9)°) and **9** (94.72(14)°) yet the C_3N_2Al ring of **3** is close to planar. Moreover, the average Al-N bond distance in **3** (1.921(2) Å) is almost the same as that for **8** (1.928(2) Å) despite the fact that the Dipp substituent is appreciably more bulky than C_6F_5. Likewise, [{(HC)(CPh)$_2$N(p-tolyl)}$AlMe_2$], with an N-Al-N bond angle of 94.94(6)°, has an essentially planar AlNCCN backbone [12]. On the other hand, [{HC)(CPh)$_2$N($SiMe_3$)$_2$}$AlMe_2$] adopts a boat conformation [13]. Finally, we note that the metrical parameters for the $AlMe_2$ moieties of **3**, **8**, and **9** are very similar.

The molecular structure of **4** (Fig. 4 and Table 1) bears a close resemblance to that of the analogous aluminum compound, **3**. Thus, in contrast to [($Dipp_2$nacnac)$GaMe_2$] (**10**), which possesses a puckered C_3N_2Ga ring [11], that of **4** is very close to planarity. In fact, within experimental error, the Ga atom lies in the extended C_3N_2 plane. The Ga-N, N-C and C-C bond distances for **4** are very similar to those for **10** and indicative of π-delocalization in the C_3N_2 fragment. The β-diketiminate [{(NC)C(CMe)$_2$-(NH)}$GaMe_2$] also has a planar GaNCCCN backbone; however, this may be a consequence of intermolecular CN···HN hydrogen bonding [14].

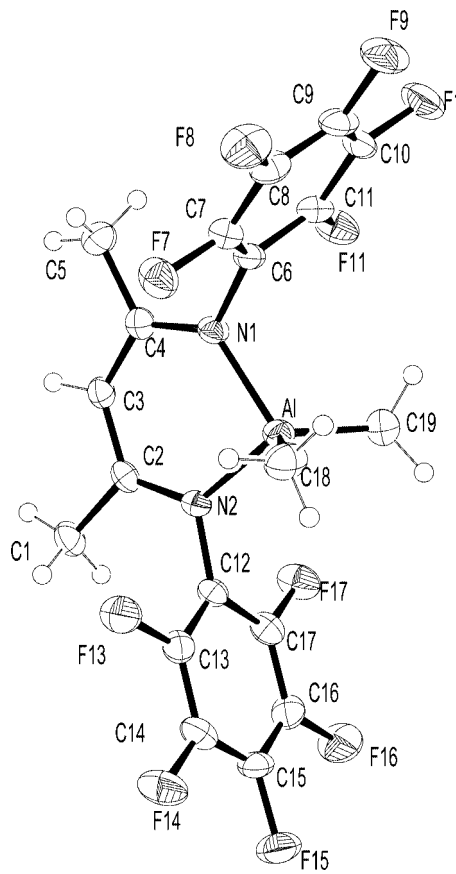

Fig. 3 Molecular structure of [{HC(CMe)$_2$(NC_6F_5)$_2$}$AlMe_2$] (**3**) showing the atom numbering scheme.Thermal ellipsoids are set to 30 % probability.

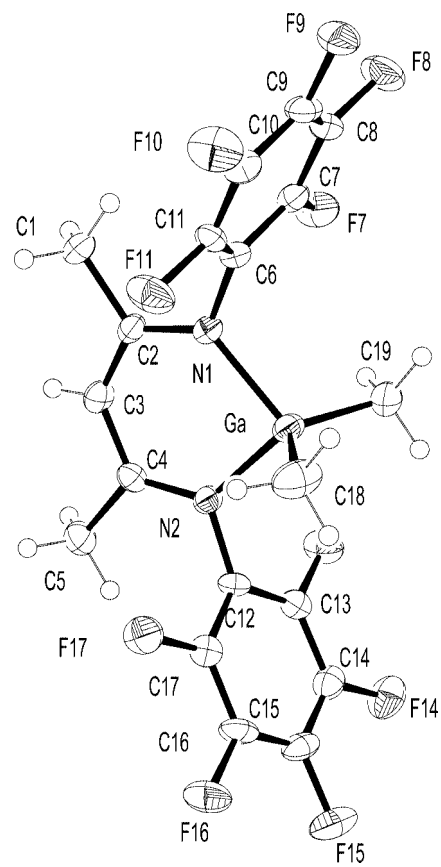

Fig. 4 Molecular structure of [{HC(CMe)$_2$(NC_6F_5)$_2$}$GaMe_2$] (**4**) showing the atom numbering scheme.Thermal ellipsoids are set to 30 % probability.

Experimental Part

Synthesis

All manipulations and reactions were performed under a dry, oxygen-free argon atmosphere or under vacuum using standard Schlenk or drybox techniques; all glassware was oven-dried before use. Toluene and pentane were distilled over sodium; both solvents were degassed prior to use. Compound **1** was prepared according to the literature method [4] and MeLi (1.6 *M* solution in Et_2O), $AlMe_3$, and $GaMe_3$ were procured commercially and used without further purification.

2: 0.740 g (1.72 mmol) of **1** was dissolved in 30 mL of hexane in a Schlenk flask. A solution of 1.08 mL of 1.6 *M* MeLi in Et_2O was added dropwise and the reaction mixture was allowed to warm to 25 °C. A crop of colorless crystals (mp 106-109 °C) formed upon storage of the reaction mixture overnight at −30 °C. The yield of **2** was essentially quantitative.

^{1}H NMR (C_6D_6) δ 4.96 (s, 1H, CH), 2.62 (q, 4H, CH_2 (Et_2O)), 1.74 (s, 6H, CMe) 0.62 (t, 6H, CH_3 (Et_2O)). **^{19}F NMR** (C_6D_6) δ −153.1 (m, 2F, *m*-F), −165.1 (m, 1F, *p*-F), −166.0 (m, 2F, *o*-F). MS (CI^+, CH_4): *m/z* 511 [M + H]$^+$. **HRMS** (CI^+, CH_4) Calc. for $C_{21}H_{18}F_{10}LiN_2O$: 511.1420. Found: 511.1417.

3: 0.282 g (0.656 mmol) of **1** and 0.0472 g (0.656 mmol) of trimethylaluminum were allowed to mix in 50 mL of toluene at 25 °C in a Schlenk flask. The resulting pale yellow reaction mixture was stirred overnight at 25 °C. Removal of the solvent and volatiles under reduced pressure afforded a 67 % yield of white solid **3** (mp 145-146 °C). Compound **3** was recrystallized from toluene.

^{1}H NMR (C_6D_6): δ 4.74 (s, 1H, CH), 1.27 (s, 6H, CMe), −0.49 (s, 6H, AlMe); **^{19}F NMR** (C_6D_6) δ −147 (m, 2F, *m*-F), −156 (t, 1F, *p*-F), −162 (m, 2F, *o*-F); **^{27}Al NMR** (C_6D_6): δ 212 (br, s). MS (CI^+, CH_4): *m/z* 487 (M^+). **HRMS** (CI^+, CH_4) Calc. for $C_{19}H_{14}AlF_{10}N_2$ 487.0813. Found: 487.0820.

4: 0.181 g (0.158 mmol) of trimethylgallium was allowed to react with 0.068 g (0.158 mmol) of **1** in 50 mL of toluene as described above for the synthesis of **3**. Removal of the solvent and volatiles resulted in a 60 % yield of white, solid **4** (mp 140-142 °C). Compound **4** was recrystallized from pentane.

^{1}H NMR (C_6D_6) δ 4.70 (s, 1H, CH), 1.32 (s, 6H, CMe), −017 (s, 6H, GaMe). **^{19}F NMR** (C_6D_6) δ −145 (m, 2F, *m*-F), −151 (t, 1F, *p*-F), −164 (m, 2F, *o*-F). MS (CI^+, CH_4): *m/z* 528 (M+). **HRMS** (CI^+, CH_4) Calc. for $C_{19}H_{14}F_{10}GaN_2$: 529.0253. Found: 529.0266.

Single crystal X-ray crystallography

Crystals of **1**−**4** of suitable quality were collected directly from a Schlenk-type flask under argon pressure, and covered immediately with degassed perfluorinated polyether oil. The X-ray data were collected on a Nonius Kappa CCD diffractometer. All four structures were solved by direct methods, and refined by full-matrix least-squares on F^2 using the SHELXTL software package [15]. A summary of crystallographic data is presented in Table 2. Note that **4** crystallizes as a racemic twin in the non-centrosymmetric space group $Pca2_1$. The refined Flack Parameter is 0.582(14).

Crystallographic data for the structures **1**−**4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 265977-265980. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax:int.code+(1223)336-033; e-mail for inquiry; fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

Spectroscopic measurements

CI mass spectra were measured on a Finnigan MAT TSQ-700 instrument. Solution-phase NMR spectra were recorded at 295 K on a GE QE-300 spectrometer (^{1}H, 300 MHz; ^{19}F, 282 MHz; ^{27}Al, 78.21 MHz) or a Varian Inova-500 spectrometer (^{1}H, 500 MHz; ^{19}F, 470 MHz; ^{27}Al, 130 MHz). All NMR samples were flame-sealed or run immediately following removal from the drybox. Benzene-d_6 was dried over sodium-potassium alloy and distilled prior to use. ^{1}H NMR spectra are reported relative to tetramethylsilane (δ 0.00) and are referenced to solvent. ^{19}F chemical shifts are reported relative to C_6F_6 (δ −162.9), and ^{27}Al chemical shifts are reported relative to $[Al(D_2O)_6]^{3+}$ (δ 0.00). Melting points were obtained in sealed capillaries under argon (1 atm) on a Fisher-Johns apparatus and are uncorrected.

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Table 2 Crystallographic data for compounds **1** − **4**.

	1	**2**	**3**	**4**
formula	$C_{17}H_8F_{10}N_2$	$C_{21}H_{17}F_{10}LiN_2O$	$C_{19}H_{13}AlC_{10}F_{10}N_2$	$C_{19}H_{13}F_{10}GaN_2$
fw	430.25	510.31	486.29	529.03
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pca2_1$
a /Å	17.084(5)	7.357(5)	9.447(5)	25.347(5)
b /Å	10.808(5)	19.517(5)	24.498(5)	9.330(5)
c /Å	19.084(5)	15.297(5)	8.594(5)	8.323(5)
β /deg	110.095(5)	94.541(5)	95.396(5)	90.0
V /Å^3	3309(2)	2189.5(17)	1980.1(16)	1968.3(16)
Z	8	4	4	4
μ (Mo-Kα) /mm^{-1}	0.182	0.154	0.204	1.500
T/K	293(2)	153(2)	153(2)	153(2)
R_1	0.0498	0.0798	0.0460	0.0392
wR_2	0.1109	0.1138	0.0881	0.0785

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