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The Fluorinated Lithiumalkoxide LiOR^F (R^F = C(CF$_3$)$_2$Mes), the Alcohol R^{F}OH and Attempts to use them as Precursors for New Weakly Coordinating Anions (WCAs)

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Abstract. The Li alkoxides [LiOR^F]$_4$ (**1**), [LiOR^F]$_4$[LiF]$_2$ (**2**) and the solvent coordinated Li-gallate Li(C$_2$H$_4$Cl$_2$)[Ga(OR^F)$_2$(Br)$_2$] (R^F = C(CF$_3$)$_2$Mes) (**3**) were prepared by reacting a stoichiometric amount of Mes-Li·OEt$_2$ and gaseous (CF$_3$)$_2$CO giving **1**. Subsequently, **2** was formed in 28 % yield in a poorly understood sequence by addition of AlBr$_3$ to **1**. Upon addition of GaBr$_3$ to four equivalents of **1** compound **3** formed. The Li alkoxide **1** forms a puckered eight membered (Li−O)$_4$ ring and compound **2** forms an almost ideal double heterocubane with a complexed Li$_2$F$_2$ four membered ring in the center. The Li-gallate **3** contains the tetrahedral anion [Br$_2$Ga(OR^F)$_2$]$^-$ and coordinates a Li(Cl$_2$C$_2$H$_4$)$^+$ cation by two contacts to the oxygen atoms of the alkoxide. The latter describes the first account of a Li-chloroalkane complex. **1** to **3** were characterized by multinuclear NMR, IR and Raman spectroscopy as well as by their single-crystal X-ray structures. It appears that the steric bulk of the OR^F alkoxide is too large to allow for the desired synthesis of the weakly coordinating anions [M(OR^F)$_4$]$^-$ (M = Al, Ga). In agreement with this, the also prepared new fluorinated alcohol HO−R^F did neither react with LiAlH$_4$ (various solvents) nor could electrochemically be reduced with H$_2$ formation (CV).

Keywords: Li alkoxide; Heterocubane; Crystal structures; Aluminum; Weakly coordinating anion (WCA)

Introduction

It has been reported that Li-containing complexes aggregate yielding ~12 general structural types [1−7]. The factors that determine the final structure of these Li species have been attributed to the choice of solvent (Lewis basicity) used during their synthesis, the electron-donating ability of the α-atom of the ligand (C, N, O or X), the bonding ability of the ligand (mono-, bi-, tri-, or polydentate), or the steric bulk and number of the ligands (−X, −OR, −NR$_2$) [1−8].

We are interested in fluorinated metal alkoxides [9, 10] as precursors to new weakly coordinating anions (WCAs) in alkoxy metalates [M(OR^F)$_4$]$^-$ [11] to complement our presently used (per-)fluorinated alkoxy residues OR^F = C(CF$_3$)$_3$, C(CF$_3$)$_2$R (R = H, Me) with the bulky OC(CF$_3$)$_2$Mes (Mes = 2,4,6-Me$_3$C$_6$H$_2$). The desired [Al(OR^F)$_4$]$^-$ WCA with R^F = C(CF$_3$)$_2$Mes appeared a valuable synthetic goal, since it should be very stable towards electrophilic attack due to the steric shielding provided by the bulky OC(CF$_3$)$_2$Mes ligand. Moreover, WCAs such as those in the aluminate Li[Al(OR^F)$_4$] [11] evoke easily accessible Li$^+$ cations, which tend to be "naked". Such weakly coordinated Li$^+$ ions may even be soluble in toluene [12] and *n*-hexane [13] and are therefore active as catalyst in organic transformations as Diels-Alder reactions, 1,4-conjungated additions and pericyclic arrangement reactions [12, 13]. The related Li[Al(OC(CF$_3$)$_2$Ph)$_4$] was shown to be a good catalyst for this purposes [13].

The most widespread synthesis [3] of Li-alkoxides LiOR is the reaction of the alkaline metals or alkaline metal hydrides with alcohols R−OH (R = organic). Due to the small and polarizing Li$^+$ ion, the structures tend to be aggregated Li$^+$X$^-$ (X = halide, OR, NR$_2$): Monomeric ion pairs of Li$^+$X$^-$ only exist in the gasphase (X = halide [14], NR$_2$ [15]), which associate in condensed phases − as ligand free systems − with formation of ring molecules (LiX)$_n$ (n = 2, 3 rarely 4 (types I, II, III), infinite chains (LiX)$_\infty$ (type IV), heterocubanes (CN$_{Li}$ = 3) (see type V), aggregated heterocubanes (type VI), ladders (type VII) or even hexagonal prisms (type VIII in Fig. 1).

Herein we report on the preparation and structural characterization of compounds containing the OR^F residue (R^F = C(CF$_3$)$_2$Mes), i.e. structural variations of LiOR^F, the alcohol HO−R^F and first attempts to use the alkoxide/alcohol for the preparation of WCAs of type [M(OR^F)$_4$]$^-$ (M = Al, Ga) by reaction with MBr$_3$/LiMH$_4$.

Results and Discussion

Syntheses

Preparation of [LiOC(CF$_3$)$_2$Mes]$_4$ (1): 1 was formed by the reaction of Mes−Li·OEt$_2$ and gaseous (CF$_3$)$_2$CO (Eq. (1)).

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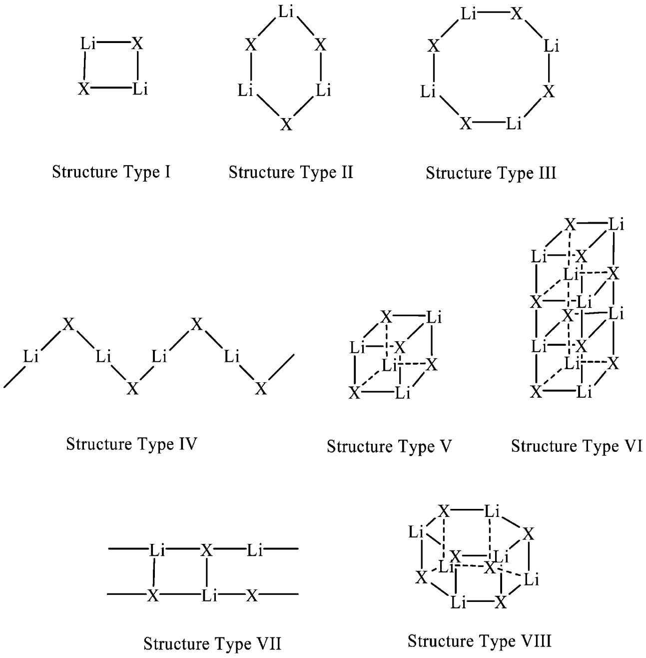


Structure Type I

Structure Type II

Structure Type III

Structure Type IV

Structure Type V

Structure Type VI

Structure Type VII

Structure Type VIII

Figure 1 General structural types of $[Li^+X^-]_n$ (X = halide, OR, NR_2; R = alkyl, aryl).

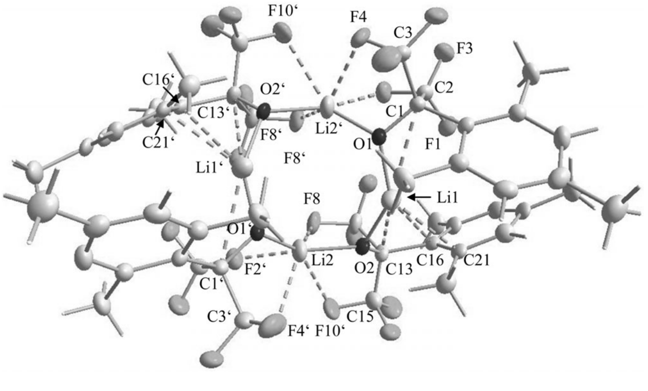
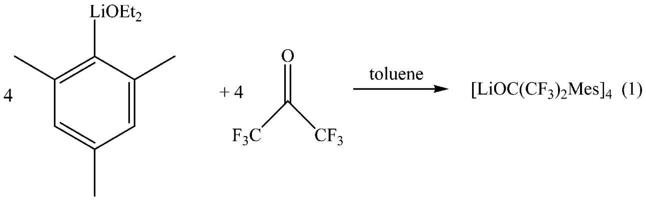


Figure 2 Molecular structure of $[LiOC(CF_3)_2Mes]_4$ (**1**) at 140 K with thermal displacement ellipsoids showing 50 % probability.

Selected bond lengths and interactions are given in Å and angles in °: Li(1)−O(1) 1.802(9), Li(1)−O(2) 1.821(9), Li(1)−C(1) 2.744(10), Li(1)−C(13) 2.681(10), Li(1)−C(16) 2.791, Li(1)−C(21) 2.597(9), Li(2)−O(1)′ 1.857(9), Li(2)−O(2) 1.852(8), O(1)−C(1) 1.364(5), C(1)−C(4) 1.567(6), O(2)−C(13) 1.361(5), C(13)−C(14) 1.561(7), C(13)−C(15) 1.546(7), C(13)−C(16) 1.562(6), Li(2)−F(2)′ 2.123(9), Li(2)−F(4)′ 2.261(10), Li(2)−F(10)′ 2.787(1), Li(2)−F(8)′ 2.155(10), $(C-F)_{av.}$ 1.331(7); O(1)−Li(1)−O(2) 138.2(5), Li(1)−O(1)−Li(2)′ 121.1(4), Li(1)−O(2)−Li(2) 115.7(4), O(2)−Li(2)−O(1)′ 127.3(5), C(1)−O(1)−Li(1) 119.5(4), C(13)−O(2)−Li(1) 114.0(4), O(1)−C(1)−C(3) 109.3(3), O(1)−C(1)−C(4) 112.0(4), C(3)−C(1)−C(4) 108.1(4), O(2)−C(13)−C(14) 104.2(3), O(2)−C(13)−C(16) 110.8(4), C(15)−C(13)−C(16) 110.2.

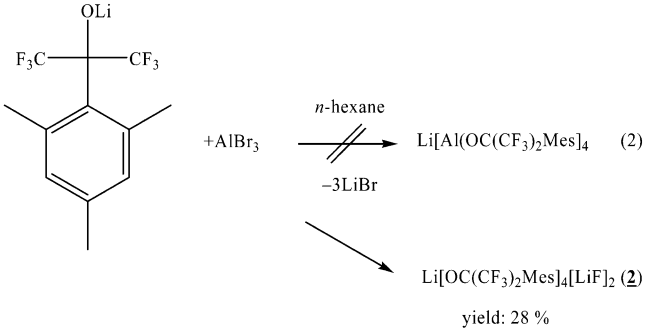
The latter was condensed onto the frozen toluene solution of $Mes-Li\cdot OEt_2$. After stirring for 4 hours at 213 K the mixture was allowed to slowly reach room temperature. The resulting light yellow solid product was washed, recrystallized from *n*-pentane, isolated, and spectroscopically characterized.



The lithium alkoxide **1** crystallizes in the rare structural type III; the central structural element is a puckered eight membered $(Li-O)_4$ ring (Fig. 2).

Thin, plate-shaped colorless crystals of $[LiOC(CF_3)_2Mes]_4$ (**1**) (Fig. 2) were obtained by crystallization of a *n*-pentane solution at 253 K. The centrosymmetric eight-membered ring consists of an alternating arrangement of Li and O atoms, where two of the four electrophilic and small Li atoms are six-coordinated (LiO_2F_4 2+4 coordination) and the other two approach a linear arrangement with some weak residual Li−Mes interactions (Li−C: 2.597−2.791 Å; 2.703 Å(av)). The tetrameric structure of this lithium organyl is untypical, since such lithium alkoxides tend to crystallize in the heterocubane $(LiOR)_4$ structure of type V. Probably the steric demand of the mesitylene residues forces the coordination of the four Li−O units into a ring shape, where the average Li−O bonds are 1.854 Å (1.802−1.857 Å). The O−Li−O bond angles are on average larger than 120° (132.8° (av)) and the Li−O−Li bond angles tend to be smaller on average than 120° (118.4° (av)). The intramolecular contact of Li(2) to one F atom of each CF_3 group (2.331 Å (av), range: 2.123 Å to 2.787 Å) elongates the corresponding C−F bond distances by 0.026 Å (av) in comparison to the other C−F bonds (1.323 Å (av)).

Preparation of $[LiOC(CF_3)_2Mes]_4[LiF]_2$ (2): 2 was formed by the reaction of $[LiOC(CF_3)_2Mes]_4$ and $AlBr_3$ in *n*-hexane at 273 K. In an poorly understood sequence an F-atom from the alkoxide is removed rather than that $AlBr_3$ reacts by metathesis to the lithium alkoxy aluminate $Li[Al(OR^F)_4]$ (R^F = $C(CF_3)_2Mes$). In the course of the decomposition the $[LiF]_2$ (**2**) complex was formed (Eq. (2)).



Further routes to Li[Al(OR^F)$_4$] (R^F = C(CF$_3$)$_2$Mes) were investigated: The reaction in toluene led to an impure and decomposed non assignable red product mixture. Several attempts with various conditions (order of adding the products, temperature, solvents) did not lead to the desired product Li[Al(OR^F)$_4$] and the only clear result was formation of **2**. Thin, plate-shaped colorless crystals of centrosymmetric [LiOC(CF$_3$)$_2$Mes]$_4$[LiF]$_2$ (**2**) (Fig. 3) were obtained by crystallization from *n*-hexane solution at 253 K.

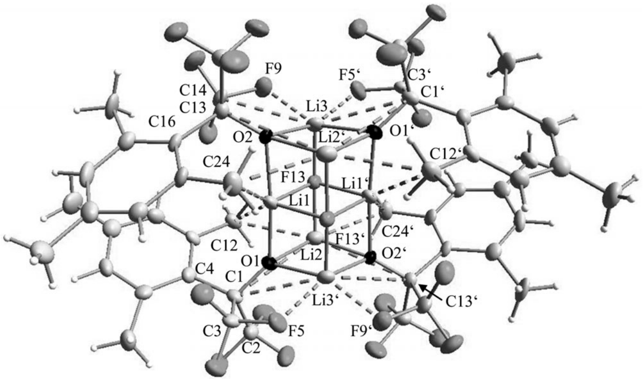
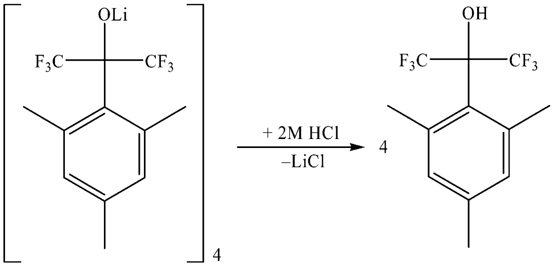


Figure 3 Molecular structure of [LiOC(CF$_3$)$_2$Mes]$_4$[LiF]$_2$ (**2**) at 140 K with thermal displacement ellipsoids showing 50 % probability.

Selected bond lengths and interactions are given in Å and angles in °: Li(1)−F(13)′ 1.940(9), Li(1)−F(13) 1.947(9), Li(1)−O(1) 1.974(9), Li(1)−O(2) 1.998(9), Li(1)−C(24) 3.273, Li(1)−C(12) 3.340, Li(2)−C(24) 2.837, Li(2)−C(12) 2.809, Li(2)−C(1) 3.133, Li(2)−C(13), Li(3) −C(14) 2.845, Li(3)−C(1) 2.894, Li(2)−F(13) 1.841(9), Li(2)−O(1) 1.919(10), Li(2)−O(2)′ 1.928(10), Li(3)−F(13) 1.843(9), Li(3)−O(1)′ 1.976(10), Li(3)−F(5)′ 1.979(9), Li(3)−F(9) 1.982(9), Li(3)−O(2) 1.986(9), F(13)−Li(1)′ 1.940(9), O(1)−C(1) 1.392(6), O(1)−Li(3)′ 1.976(10), O(2)−C(13) 1.373(6), O(2)−Li(2)′ 1.928(10), C(1)−C(2) 1.549(7), C(1)−C(3) 1.568(7), C(1)−C(4) 1.572(7); F(13)′−Li(1)−F(13) 86.6(4), F(13)′−Li(1)−O(1) 93.4(4), F(13)−Li(1)−O(1) 90.3(4), F(13)′−Li(1)−O(2) 90.7(4), F(13) −Li(1)−O(2) 92.4(3), O(1)−Li(1)−O(2) 175.1(5), F(13)−Li(2)−O(1) 95.4(4), F(13)−Li(2)−O(2)′ 96.1(4), O(1)−Li(2)−O(2)′ 102.2(4), F(13)−Li(3)−O(1)′ 96.5(4), F(13)−Li(3)−F(5)′ 106.9(4), O(1)′−Li(3)−F(5)′ 79.0(4), F(13)−Li(3)−F(9) 112.9(5), O(1)′−Li(3)−F(9) 150.6(5), F(5)′−Li(3)−F(9) 92.8(3), F(13)−Li(3)−O(2) 96.0(4), O(1)′−Li(3)−O(2) 98.1 (4), F(5)′−Li(3)−O(2) 157.1(5), F(9)−Li(3)−O(2) 78.5(3), Li(1)′−F(13)−Li(1) 93.4(4), Li(2)′−O(2)−Li(3) 79.0(4), Li(2)′−O(2)−Li(1) 84.4(4), Li(3)−O(2)−Li(1) 83.0(4), O(1)−(1)−C(2) 107.8(4), O(1)−C(1)−C(3) 104.1(4), C(2)−C(1)−C(3) 107.8(4), O(1)−C(1)−C(4) 111.9(4), C(2)−C(1)−C(4) 110.7(4), C(3)−C(1)−C(4) 114.1(4), O(2)−C(13)−C(16) 111.9(4), O(2)−C(13)−C(14) 103.9(4), C(16)−C(13)−C(14) 115.0(4).

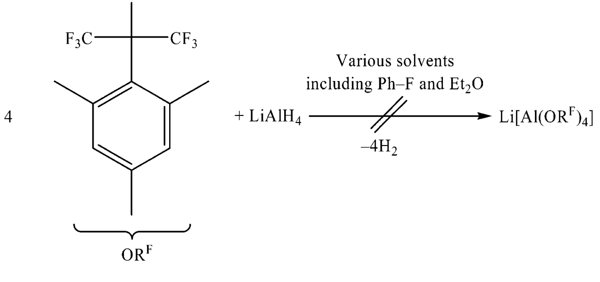
The asymmetric unit consists of two lithium alkoxy- and one lithium fluoride formula units, where the twelve Li−O bonds and eight Li−F bonds of the symmetry generated complete molecule form an almost ideal double heterocubane with an average Li−O bond distance of 1.964 Å (1.919−1.986 Å) and two short Li-F distances at 1.841 and 1.843 Å as well as two longer at 1.940 and 1.947 Å. The O−Li−O angles of each cube are larger (98.1−102.2°, 100.2° av) than the Li−O−Li angles (79.0−84.4°, 82.1° av). Also the O(1)−Li(1)−O(2) angle of 175.1° along the centerline proves the slight distortion of this double cage. The two central cubes are each shielded by two C(CF$_3$)$_2$Mes groups, where one F atom of every second CF$_3$ group forms an intramolecular Li−F contact (1.979 Å and 1.982 Å). Several weak residual Li−Mes interactions saturate the six times coordinated Li(1) (Li−C: 3.273−3.340 Å (3.307 Å(av)) and the seven times coordinated Li(2) and Li(3) (Li−C: 2.837−3.178 Å (2.949 Å(av)). The numerous Li−F contacts are in very good agreement with other known structures of fluorinated lithium [1] and the homologous sodium alkoxides [16−18] In the comparable heterocubane structure of (LiOR′)$_4$ (R′ = C(CF$_3$)$_3$) [10] the analogous Li−F contacts are longer and at 2.42 Å (av) [10].

Preparation of HOC(CF$_3$)$_2$Mes. The general idea of the preparation of the alcohol HOC(CF$_3$)$_2$Mes was to achieve the synthesis of the lithium alkoxyaluminate Li[Al(OR^F)$_4$] (R^F = C(CF$_3$)$_2$Mes) by reaction with LiAlH$_4$ in analogy to published procedures [11, 13]. The alcohol was formed by the acidic hydrolysis (2M HCl) of the fluorinated lithium alkoxide LiOC(CF$_3$)$_2$Mes under normal atmospheric conditions. The alcohol was separated from the aqueous phase by extraction with fluorobenzene. Then the alcohol was distilled, (b.p. = 393 K, 0.01 mbar, inert conditions), dried and isolated as a colorless liquid (yield: 28 %).



(3)

The spectroscopic analyses of HO−C(CF$_3$)$_2$Mes are as expected. Moreover, a cyclovoltammogram of the alcohol in the solvent mixture PC:EC:DMC:toluene = 20:20:50:10 in 1M LiPF$_6$ was recorded. It was observed that, even at very low potentials, during reduction no evolution of hydrogen occurred. This unusual behavior was ascribed to the bulkiness of R^F and is in agreement with the inertness towards reaction with LiAlH$_4$. Accordingly, the proposed synthesis of Li[Al(OR^F)$_4$] (Eq. 4) did not lead to success, no reaction could be observed.



(4)

Further attempts to prepare $Li[Al(OR^F)_4]$ were also done in Et_2O with dissolved $LiAlH_4$, but no reaction was observed. Overall, it appears that the novel R^F residue is too bulky to coordinate four times to the (smaller) aluminum atom. Even coordinating solvents like Et_2O did not support to the formation of $Li[Al(OR^F)_4]$ from $LiAlH_4$ and 4 R^F−OH.

Preparation of $Li(C_2H_4Cl_2)[Ga(OC(CF_3)_2Mes)_2(Br)_2]$ (3). It was tried to synthesize the analogous lithium alkoxygallate as in equation 2, but replacing $AlBr_3$ for $GaBr_3$. Gallium is a bit larger than aluminum and a somewhat weaker Lewis acid, so it was hoped to overcome the fluoride abstraction as found by reaction with $AlBr_3$. However, the synthesis only led to the mixed bromo-alkoxy-gallate **3**. Although fluoride abstraction did not occur, it appears that the OR^F residue is also too bulky for Gallium to form the tetrasubstituted $[Ga(OR^F)_4]^-$ structure. Colorless crystals of $Li(C_2H_4Cl_2)[Ga(OC(CF_3)_2Mes)_2(Br)_2]$ (**3**) (Fig. 4) were obtained by crystallization from a dichloroethane solution at 253 K in good yield. The solid-state structure contains half a molecule in the asymmetric unit. The central structural feature of **3** is a centrosymmetric, almost square planar $Li\text{-}O_2Ga$ ring, which contains a lithium atom that is additionally coordinated by one solvent molecule dichloroethane. The Li−O distance is 1.995 Å, the Ga−O distance is 1.883 Å.

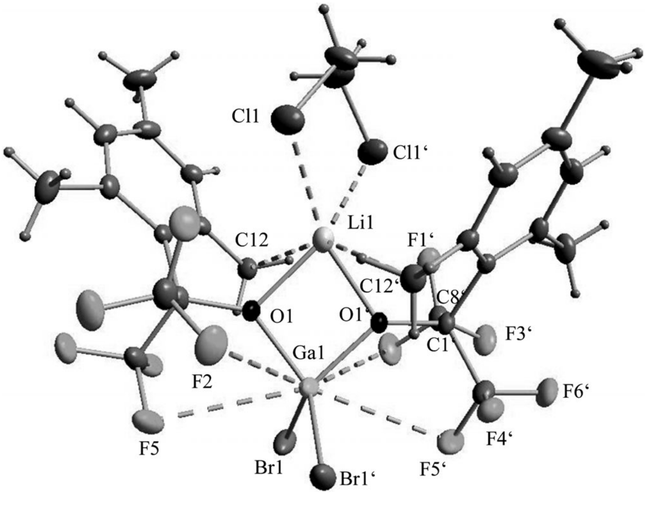


Figure 4 Molecular structure of $Li(C_2H_4Cl_2)[Ga(OC(CF_3)_2\text{-}Mes)_2(Br)_2]$ (**3**) at 140 K with thermal displacement ellipsoids showing 50 % probability.

Selected bond lengths and interactions are given in Å and angles in °: Li(1)−O(1) 1.991(5), Br(1)−Ga(1) 2.3088(4), Ga(1)−O(1) 1.8832(17), Cl(1)−C(13) 1.782(3), Cl(1)−Li(1) 2.641(5), Li(1)−C(12) 2.945, Ga(1)−F(2) 3.189, Ga(1)−F(5) 3.139, O(1)−C(1) 1.406(3); O(1)′−Ga(1)−O(1) 85.07(11), O(1)′−Ga(1)−Br(1)′ 113.23(5), O(1)−Ga(1)−Br(1)′ 118.48(5), Br(1)′−Ga(1)−Br(1) 107.52(2), C(13)−Cl(1)−Li(1) 105.67(14), Ga(1)−O(1)−Li(1) 97.72(14), O(1)−Li(1)−O(1)′ 79.5(3), O(1)−Li(1)−Cl(1) 110.30(6), O(1)′−Li(1)−Cl(1) 149.05(6), Cl(1)−Li(1)−Cl(1)′ 76.88(18), C(1)−O(1)−Li(1) 125.1(2), O(1)′−Ga(1)−Li(1) 42.54(5), O(1)−Li(1)−Ga(1) 39.74(13).

The slightly distorted square exhibits an O−Ga−O angle that is larger (85.07°) than the O−Li−O angle (79.5°). Both are smaller than the Li−O−Ga angle (97.72°). The two remaining free coordination sites of the sixfold coordinated Li and eightfold coordinated Ga atoms are occupied by a $C_2H_4Cl_2$ molecule (coordinated via the Cl atoms), two Br atoms and two weak Li−C contacts (Li−C: 2.945 Å) as well as four weak Ga−F contacts (Ga-F: 3.139-3.189 Å (3.164 Å(av)). The C-Cl bond lengths in the coordinated $C_2H_4Cl_2$ molecule are with 1.781 Å similar to the distance of 1.791 in free $C_2H_4Cl_2$ [19]. The Ga−Br (2.309 Å) and the Ga−O distances are similar and in good agreement to the Ga−Br bond lengths in $[GaBr_4]^-Ph_2PPPh_3^+$ [20] (2.322 Å av) and to the Ga−O distances (1.883 Å) in $[Ga(\mu\text{-}OCMe_2Et)(OCMe_2\text{-}Et)_2]_2$ (=**A**) (1.811 Å av) [21] This also fits to the (Li−O−Ga−O) ring in $[Li(THF)_2][GaN(SiMe_3)_2(OSiMe_3)_2Cl]$ (=**B**), where the the Li−O (1.983 Å) and Ga−O (1.872 Å) bond lengths are nearly equivalent [22]. In **3** it appears that the small and hard Li^+ cation coordinates more readily to the harder O-atoms (and not to the softer and much more accessible Br-atoms).

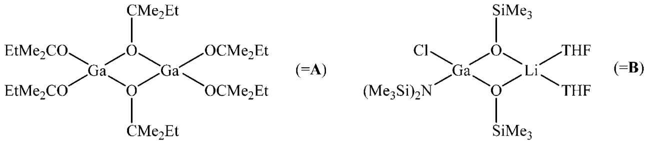


Figure 5 Structures of $[Ga(\mu\text{-}OCMe_2Et)(OCMe_2\text{-}Et)_2]_2$ (=**A**) [21] and $[Li(THF)_2][GaN(SiMe_3)_2(OSiMe_3)_2Cl]$ (=**B**) [22] compared to **3**.

Conclusion

The complete structural characterizations of $[LiOC(CF_3)_2Mes]_4$ (**1**), $[LiOC(CF_3)_2Mes]_4[LiF]_2$ (**2**) and $Li(C_2H_4Cl_2)[Ga(OC(CF_3)_2Mes)_2(Br)_2]$ (**3**) were achieved. **1** could be prepared in large scale and with excellent yields; it is a rare example of a Li-alkoxide that does **not** adopt a heterocubane structure. As a side reaction with $AlBr_3$, the LiF-complex **2** with a double heterocubane structure formed. The alkoxide could be readily hydrolyzed to the respective bulky alcohol, which did **not** react with $LiAlH_4$ and did **not** liberate H_2 upon electrochemical reduction. All attempts to synthesize WCAs from these starting materials failed: reactions to prepare $Li[Al(OR^F)_4]$ from $AlBr_3$ or $LiAlH_4$ did not lead to success. Apparently the bulk of the $C(CF_3)_2Mes$ residue is to large to allow incorporation to the desired aluminate. Similarly, the respective $[Ga(OR^F)_4]^-$ could not be prepared and only the disubstituted dichloroethanecomplex **3** could be isolated. According to a search in the CSD database, the latter is the first account of a Li-Chloroalkane complex. Complex **3** shows that the hard Li^+ cation prefers coordination of the hard but poorly accessible oxygen atom over the soft but easily accessible bromine atoms.

Experimental Section

General Procedures: Due to the air- and moisture-sensitivity of most materials all manipulations were undertaken using standard vacuum and Schlenk techniques as well as in a glove box with a argon atmosphere (H_2O and O_2 <1 ppm). All solvents were dried by conventional drying agents, distilled and stored under argon. Solution NMR spectra for substance **1** and **2** were recorded in [D_8]toluene, for substance **3** in $CDCl_3$ at room temperature on a Bruker 400 MHz spectrometer; data are given in ppm relative to the residual internal solvent signals (^{1}H, ^{13}C) or external $FCCl_3$ (^{19}F). IR spectra of substance **1**, **2** and **3** were obtained in Nujol mulls between CsI plates on a Bruker Vertex 70 IR spectrometer, Raman spectra were recorded on a Bruker RAM II Raman module using a highly sensitive Ge detector.

Synthesis of $[LiOC(CF_3)_2Mes]_4$ (1). In a 500 ml two necked round bottom flask connected to a dropping funnel and a gas cooler 30 g (0.150 mol) colorless $Mes{-}Li \cdot OEt_2$ were dissolved in approximately 80 ml of toluene. Then 32.37 g (0.195 mol, 1.3 eq., excess) $(CF_3)_2CO$ were condensed onto the frozen solution at 77 K. The mixture was allowed to reach 213 K, whereby the gas cooler was set with a cryostat to a temperature of 203 K. After stirring for 4 hours at 213 K the mixture was allowed to reach room temperature. Then the overlaying solution was decanted from the light yellow solid product. This was isolated, washed with pentane, recrystallized from toluene at 253 K, isolated and dried by vacuum distillation. The resulting colorless product (yield: 43.10 g, 98 %) was assigned by X-ray diffraction and spectroscopy as $[LiOC(CF_3)_2Mes]_4$.

^{1}H NMR (400 MHz, [D_8]toluene, 298 K) δ = 1.74 (s, 3H, $-CH_3$ (ortho)), 2.29 (s, 3H, $-CH_3$ (para)), 2.50 (s, 3H, $-CH_3$ (ortho)), 6.44 (s, 1H), 6.51 (s, 1H); **^{19}F NMR** (376 MHz, [D_8]toluene, 298 K) δ = −68.0 (s, 6F, 2x $-CF_3$); **^{7}Li NMR** (156 MHz, [D_8]toluene, 298 K) −7.9 (s, 1Li); **IR** (CsI plates, Nujol, 298 K)/cm^{-1}: ν = 668 s, 678 w, 711 s, 743 w, 747 w, 851 m, 858 w, 898 s, 931 s, 951 vs, 968 m, 1041 m, 1100 s, 1119 s, 1142 vs, 1156 vs, 1175 s, 1196 s, 1205 s, 1224 vs, 1265 s, 1286 s, 1362 m, 1375 m, 1387 m, 1395 m, 1419 m, 1436 m, 1457 m, 1465 m, 1473 m, 1489 m, 1497 m, 1507 m, 1521 m, 1540 s, 1559 s, 1570 m, 1576 m, 1616 m, 1624 m, 647 m, 1653 s, 1663 m, 1670 m, 1684 m, 1700 m, 1717 m, 1734 m, 1740 m, sh., 1751 m, 1772 m, 1792 m, 2964 s; **Raman** (298 K)/cm^{-1}: 521 (33), 541 (55), 572 (62), 595 (29), 748 (64), 975 (19), 1103 (31), 1170 (16), 1282 (24), 1376 (36), 1385 (40), 1445 (19), 1465 (19), 1566 (14), 1613 (43), 2868 (27), 2923 (100), 2982 (52), 2995 (45), 3009 (36), 3022 (43) [(%)].

Synthesis of $HOC(CF_3)_2Mes$. For the hydrolysis (no inert conditions) of 10 g (34.23 mmol) $LiOC(CF_3)_2Mes$, approximately 20 ml of 2M HCl were given to the salt. Then the mixture was stirred for half an hour and afterwards the resulting alcohol separated from the aqueous phase by adding three times about 40 ml fluorobenzene to the liquid. The organic phase turned light yellow and was then dried for three hours over about 50 g $CaCl_2$. After filtration and distillation (bp. of $HOC(CF_3)_2Mes$: 393 K, 0.1 mbar), drying over P_2O_5 and condensation, the alcohol $HOC(CF_3)_2Mes$ was isolated as a colourless liquid (yield: 2.70 g, 28 %) and then spectroscopically analyzed.

^{1}H NMR (400 MHz, [D_8]toluene, 298 K) δ = 2.07 (3H, $-CH_3$ (ortho)), 2.47 (s, 3H, $-CH_3$ (para)), 2.64 (s, 3H, $-CH_3$ (ortho)), 2.77 (s, 1H $O{-}H$), 6.68 (s, 1H), 6.78 (s, 1H); **^{19}F NMR** (376 MHz, [D_8]toluene, 298 K) δ = −77.3 (s, 6F, 2x $-CF_3$); **IR** (CsI plates, nujol, 298 K)/cm^{-1}: ν = 485 w, 513 w, 548 w, 590 w, 635 w, 707 s, 741 m, 752 m, 853 m, 890 s, 926 m, 955 s, 983 m, sh., 1098 m, 1127 vs, 1169 m, 1198 vs, 1238 vs, 1386 w, 1459 m, 1486 m, 1570 w, 1613 m, 2929 w, 3537 m, 3610 m.

Synthesis of $[LiOC(CF_3)_2Mes]_4[LiF]_2$ (2). 3.947 g (13.510 mmol) of $[LiOC(CF_3)_2Mes]_4$ were given into a 250 ml round bottom flask, connected to a dropping funnel. Then, under stirring, approximately 30 ml *n*-hexane was given to the powder at 273 K. Only half of the lithium alkoxide was soluble in the solvent. Afterwards 0.90 g (3.378 mmol) $AlBr_3$ was given at once to the mixture, whereby it turned dark red. It was refluxed for two hours and then the dark solid decanted from the colorless solution, which was isolated, concentrated and crystallized at 253 K. The precipitated crystals were spectrocopically and structurally assigned to $[LiOC(CF_3)_2Mes]_4[LiF]_2$ (yield$_{crystals}$: 0.871 g, 21 %). **^{1}H NMR** (400 MHz, [D_8]toluene, 298 K) δ = 1.89 (3H, $-CH_3$ (ortho)), 2.26 (s, 3H, CH_3 (para)), 2.34 (s, 3H, CH_3 (ortho)), 6.51 (s, 1H), 6.58 (s, 1H); **^{19}F NMR** (376 MHz, [D_8]toluene, 298 K) δ = −73.4 (s, 24F, 4x $-CF_3$) (a signal for $Li{-}F$ could not be detected), **^{7}Li NMR** (156 MHz, [D_8]toluene, 298 K) −2.1 (s, br., 6Li); **IR** (CsI plates, Nujol, 298 K)/cm^{-1}: ν = 473 w, 538 w, 589 w, 616 w, 670 w, 708 m, 720 m, 741 m, 750 m, 850 m, 897 s, 930 m, 953 s, 1038 m, 1097 m, 1128 m, 1158 m, 1198 s, 1236 s, 1263 s, 1284 m, sh., 1329 m, sh., 1377 vs, 1461 vvs, 2975 w.

Synthesis of $Li(C_2H_4Cl_2)[Ga(OC(CF_3)_2Mes)_2(Br)_2]$ (3). In a 250 ml two necked round bottom flask connected to a dropping funnel 0.40 g (1.283 mmol) $GaBr_3$ dissolved in approximately 1 ml toluene and were added to a solution of 1.50 g (5.134 mmol) $LiO(CF_3)_2Mes$ in approximately 15 ml toluene at 213 K. Then the mixture was slowly warmed up to room temperature over night. The solution was decanted from the precipitate (probably LiBr: 0.10 g, 1.151 mmol), concentrated and crystallized from $C_2H_4Cl_2$ at 253 K. The resulting crystals were spectroscopically and structurally assigned as $Li(1,2Cl_2C_2H_4)[(Mes(CF_3)_2CO)_2GaBr_2]$ (yield$_{crystals}$: 0.72 g, 46 %).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.22 (s, 6H, 2x $Mes{-}CH_3$), 2.40 (s, 6H, 2x $Mes{-}CH_3$), 2.60 (s, 2H, $-CH_2CH_3$), 2.71 (s, 3H, $-CH_2CH_3$), 3.37 (s, 2H, H_2O (trace)), 3.72 (s, 6H, 2x $Mes{-}CH_3$), 6.91 (s, 2H, $Mes{-}H$); **^{19}F NMR** (377 MHz, $CDCl_3$, 298 K) δ = −69.5 (s, 12F, 2x $-C(CF_3)_2Mes$; **^{7}Li NMR** (156 MHz, 298 K) δ = −3.2 (s, 1Li); **IR** (CsI plates, Nujol)/cm^{-1}: ν = 417 w, 485 w, 498 w, 536 m, 543 m, 581 m, 597 w, 645 w, 660 w 679 m, 702 s 714 s, 745 m, 755 m, 867 s, 903 s, 935 s, 959 s, 976 w, sh., 1038 m, 1087 vs, 1130 vs, 1200 vs, 1217 vs, 1238 vs, 1251 vs, 1381 w, 1429 w, 1485 m, 1497 s, 1569 w, 1613 s, 2973 s; **Raman** (298 K)/cm^{-1}: ν = 174 (100), 191 (96), 218 (35), 229 (29), 240 (sh., 19), 283 (31), 325 (23), 315 (19), 336 (18), 347 (12), 377 (9), 400 (12), 411 (10), 545 (30), 555 (30), 575 (24), 598 (13), 649 (13), 662 (18), 703 (10), 722 (5), 755 (19), 763 (20), 980 (16), 1108 (12), 1137 (7), 1148 (12), 1210 (11), 1287 (13), 1383 (24), 1433 (9), 1470 (20), 1573 (8), 1616 (32), 2741 (5), 2761 (5), 2925 (60), 2960 (79), 2999 (40), 3008 (38), 3047 (36) [(%)].

X-ray Structure Determination

Crystals of **1**, **2** and **3** were obtained as described above. Data were collected on a Bruker Kappa Apex II diffractometer using Mo-Kα radiation (λ = 0.71073 Å) at T = 140 K and 100 K. Single crystals were mounted in perfluoroetheroil on top of a glass fiber and then placed in the cold stream of a low-temperature device so that the oil solidified. Unit-cell parameters were calculated from a least-squares refinement of the setting angles of 5000 reflections collected. The space groups were identified as *Pbcn* (**1**), $P2_1/c$ (**2**) and $P4_12_12$ (**3**). The structure were solved with direct methods in SHELXS [23] and successive interpretation of the difference Fourier maps using SHELXL-97. Refinement against F^2 was carried out with SHELXL-97. All non-hydrogen atoms were included anisotropically into the refinement; all hydrogen atoms were included isotropically at the calculated positions based on a riding model. Crystal structure determination of **$[LiOC(CF_3)_2Mes]_4$ (1)**: T = 140(2) K, Lorentz polarization correction, monoclinic, *Pbcn*, Z = 4, a = 11.1781(8) Å, b = 15.3994(7) Å, c = 28.4597(13), α = 90°, β = 90°, γ = 90°, V = 4898.9(5) Å^3, μ = 0.160 mm^{-1}, ρ_{calc} =

1.584 Mg/m^3, θ_{max} = 25.03°, reflections: 28669 collected, 4216 unique (R_{int} = 0.1289), R_1 = 8.35 %, wR_2(all data) = 0.2178, GOF = 1.124. **[$LiOC(CF_3)_2Mes$]$_4$[LiF]$_2$ (2)**: T = 140(2) K, Lorentz polarizationand numerical absorption corrections Tmin/Tmax = 0.35396/1.00000, orthorhombic, $P2_1/c$, Z = 2, a = 14.7855(10) Å, b = 11.8441(7) Å, c = 14.6062(10), α = 90°, β = 99.535(7)°, γ = 90°, V = 2522.5(3) Å^3, μ = 0.163 mm^{-1}, ρ_{calc} = 1.607 Mg/m^3, θ_{max} = 25.03°, reflections: 15376 collected, 4371 unique (R_{int} = 0.1144) R_1 = 7.05 %, wR_2(all data) = 0.1994, GOF = 1.053. **$Li(C_2H_4Cl_2)[Ga(OC(CF_3)_2Mes)_2(Br)_2]$ (3)**: T = 100(2) K, Lorentz polarization and numerical absorption corrections Tmin/Tmax = 0.65857/1.00000, tetragonal, $P4_12_12$, Z = 4, a = 11.1582(10) Å, b = 11.1582(10) Å, c = 26.1495(16), α = 90°, β = 90°, γ = 90°, V = 3255.8(5) Å^3, μ = 3.558 mm^{-1}, ρ_{calc} = 1.848 Mg/m^3, $2\theta_{max}$ = 27.51°, reflections: 125178 collected, 3741 unique (R_{int} = 0.0572) R_1 = 2.90 %, wR_2(all data) = 0.0559, GOF = 1.213, the refined Flack parameter equals to 0.078(8). Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre: CCDC 655228 (**2**), 655229 (**1**), 655230 (**3**). 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)

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