Lithium Carbenoids

DOI: 10.1002/anie.201406564

# Solid-State Structure of a Li/F Carbenoid: Pentafluoroethyllithium**

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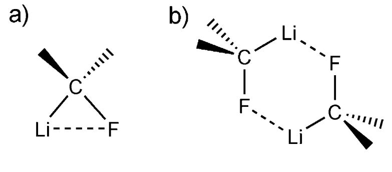
*Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday*

**Abstract:** *Lithium carbenoids are versatile compounds for synthesis owing to their intriguing ambiphilic behavior. Although this class of compounds has been known for several years, few solid-state structures exist because of their high reactivity and often low thermal stability. Using cryo X-ray techniques, we were now able to elucidate the first solid-state structure of a Li/F alkyl carbenoid, pentafluoroethyllithium ($LiC_2F_5$), finally yielding a prototype for investigating structure—reactivity relationships for this class of molecules. The compound forms a diethyl ether-solvated dimer bridged by a rare C–F–Li link. Complementary NMR spectroscopy studies in solution show dynamic processes and indicate rapid exchange of starting material and product. Theoretical investigations help to understand the formation of the observed unusual structural motif.*

Lithium carbenoids have fascinated chemists for several decades. The term carbenoid[1,2] was coined following the pioneering work of Simmons and Smith.[3] It points to their reactivity as carbene synthons[4] as a result of their structure with geminal metal atoms and electronegative atoms (O, N, halogen). Their high reactivity and their ambiphilic behavior as nucleophiles and electrophiles at the same time give them synthetic value for C–C and C–heteroatom bond formation. Examples of their use include cyclopropanation or homologation reactions, sometimes in combination with catalytic pathways.[5] Their very special nature of bonding has been the subject of considerable interest and debate up to now.[6] The most simple and extreme examples are the lithium halogen carbenoids, $R_2C(Li)X$. These prototypical geminal systems show intriguing interactions between two chemically very distinct substituents bound to the same atom.

Sound experimental knowledge of carbenoids, in particular lithium/fluorine carbenoids remains scarce—despite many theoretical contributions and some contributions to the structural chemistry of lithium carbenoids.[7] Herein we now present the first solid-state structure of a Li/F-carbenoid, namely that of pentafluoroethyllithium, $LiC_2F_5$.[8] This perfluorinated lithium alkyl has proven to be a versatile building block and of interest to both industrial synthesis and academic research.[9] Potential applications of $LiC_2F_5$ include the synthesis of novel lithium-battery electrolytes, ionic liquids, and the introduction of extremely electronegative groups generally, for instance for new phosphanes used in catalysis.[10,11] Compared to derivatives of longer perfluoroalkyl groups, pentafluoroethyl compounds are less toxic. Despite $LiC_2F_5$'s relative stability, compared to the elusive $CF_3Li$ which eliminates LiF at temperatures below −100 °C,[12] violent decompositions were reported for the preparation of $LiC_2F_5$ from $C_2F_5Cl$/*n*BuLi mixtures.[13] Because $LiC_2F_5$ is potentially explosive, it should only be handled well below −60 °C for a limited time and only in ethereal solution. Solutions decompose at higher temperatures and quickly above −40 °C. $LiC_2F_5$ has never been isolated before. Compared to the synthetically almost inaccessible $CF_3Li$[14] which easily generates the stabilized singlet carbene $F_2C$:, $LiC_2F_5$ is more stable because the carbene $F_3C(F)C$: is less stabilized and therefore its formation less favored.

An extreme description of carbenoids is: carbenes being coordinated to a Li–X unit. A number of theoretical investigations initially seemed to support this interpretation. A molecular description of the basic representative $LiCH_2F$ by quantum chemical methods showed it to adopt the structure of a three-membered ring with pronounced Li···F interactions (Scheme 1 a).[15] Concerted transfer mechanisms of the carbene fragments onto substrates, such as ethane, were discussed.[16] Numerous theoretical studies also deal with the system $LiCF_3$.[14]



*Scheme 1.*

A preformed lithium fluoride unit within the molecule has remained a guiding principle in discussion of their reactivity for long time and has found its way into text books and thereby coined the thinking of generations of chemists. This view was supported by structures of other geminal systems with unequal bonding partners, namely oxenoids and nitre-

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[**] We are grateful to Solvay GmbH (Hannover (Germany)) for providing pentafluoroethane.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201406564.

noids, with O and N atoms linking electronegative and electropositive partners. Examples of three-membered rings with a highly ionic or dative bond between electronically opposing substituents include: the peroxide *t*BuOOLi with Li-O-O rings,[17] hydrazides, such as $(Me_3Si)_2NN(SiMe_3)Li$ with Li-N-N rings,[18] and Si-O-N rings, for example, in $F_3SiONMe_2$,[19] or B-C-N rings for example, in $(F_3C)_2BCH_2NMe_2$.[20]

It was recognized early on that real lithium halogen carbenoids must necessarily be aggregated or solvated as is usually the case for lithium compounds including the alkyls.[21] The often very limited thermal stability of carbenoids and related species and their high reactivity necessitates their use in situ. This has the consequence that experimental structure elucidation was often hampered—in particular that of Li/halogen carbenoids. Despite these limitations, solvated structures of true lithium/halogen carbenoids have been determined by Boche et al. for the vinyl carbenoid 1-chloro-2,2-bis(4-chlorophenyl)-1-lithio-ethene·TMEDA·2 THF, ($sp^2$ carbon atom)[22] and the alkyl carbenoid $LiCHCl_2 \cdot 3$ pyridine.[23]

Bulky donor substituents stabilize carbenoids and this concept allowed some room-temperature examples to be generated, albeit with decreased reactivity.[24] They contain tetrahedral carbon atoms and lithium atoms of coordination numbers 5 and 4, coordinatively saturated by solvent molecules. A magnesium/bromine vinyl-type carbenoid has also been investigated.[25] All these studies demonstrated the marked lengthening of the C−X bonds in carbenoids, despite the absence of direct strong Li–X interactions.

Impressive NMR spectroscopic investigations in solution have been carried out by Seebach et al. on isotope-labeled carbenoids with Cl, Br, and I atoms.[26] Coupling patterns between $^6Li$ as well as $^7Li$ and $^{13}C$ have provided insight into the Li−C bonds but remained inconclusive regarding the aggregation motif. Notwithstanding, Seebach intuitively postulated the possibility of the formation of dimers, with halogen–lithium bonds formed in competition with solvation. Such dimers contain $Li_2C_2X_2$ rings (Scheme 1 b). Calculations on oversimplified models (no solvent, simplistic solvation models, three-coordinate Li atoms) have indicated that such aggregates might be energetically favorable.

Crystals of $LiC_2F_5$ were obtained by deprotonation of $C_2F_5H$, with *n*BuLi at −60 °C in ethereal solution (Scheme 2) and subsequent storage of the reaction mixture at −80 °C. The thermal stability limit of −40 °C required selecting and preparing the single crystals under continuous cooling. X-ray diffraction data[27] were measured using a crystal in a nitrogen cryostream. $LiC_2F_5$ crystallizes with two diethyl ether molecules completing the coordination sphere of the lithium atoms to tetracoordination. It adopts a dimeric structure (Figure 1) arranged about a center of inversion (similar to a recently reported lithiated oxirane[28]).

$$C_2F_5H + n\text{-BuLi} \xrightarrow[-\,n\text{-BuH} \; -\,60\,°C]{Et_2O} LiC_2F_5$$

*Scheme 2.* Preparation of pentafluoroethyllithium.

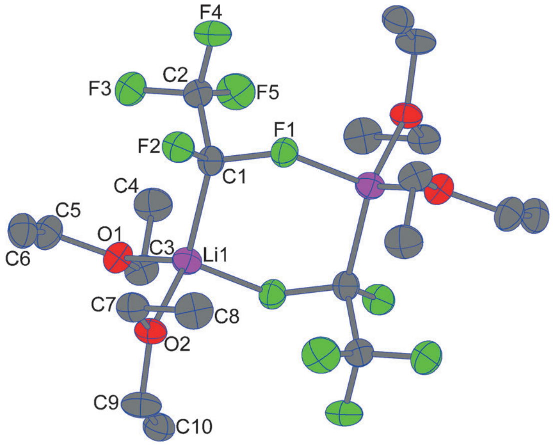
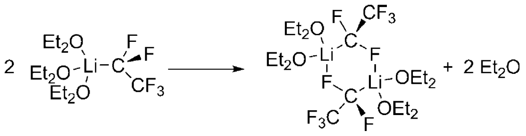


*Figure 1.* Molecular structure of $[LiC_2F_5 \cdot 2\,Et_2O]_2$ in the solid state.

The molecules are bridged not only by Li–C but also by Li–F contacts. The Li–F contact is a rare structural motif in organolithium chemistry.[29] Consistent with predictions for carbenoid structures both C−F bonds at the carbanionic site are elongated (opposite to carbanions with typical acceptor substituents). Compared to $C_2F_5H$ which has a C−F bond length of 1.35 Å at $C_\alpha$, and the C−F bond lengths of the $CF_3$ group in $LiC_2F_5$ which are in the same range, the bond C1−F2 in $LiC_2F_5$ is elongated to 1.416(2) Å and that of C1−F1 even more so to 1.465(2) Å.[30] C1−F1 is the bond to the fluorine atom forming the ring by bonding to the lithium atom. The distance between Li1 and the corresponding carbanion site C1 is 2.181(4) Å and thus comparable to the Li–C distances in above mentioned Li/Cl alkyl (2.105(9) Å) and Li/Cl vinyl (C1–Li1 2.15(1) Å) carbenoids. Surprisingly, this is markedly longer than the Li1–F1 distance at 1.957(4) Å in the same crystal, which could be expected to be dative and thus weaker. A search of dative Li⋯F distances in the Cambridge Database classifies the Li1–F1 distance as one of the shortest and close to the minimum (a Li—F contact of 1.896 Å[31] for a lithium atom coordinated by three $(F_5C_6)_4B^-$ ions). Other examples for Li–F contacts of lithium atoms bound to carbanions are rarely observed.[32]

The angles at lithium are surprisingly close to the ideal tetrahedral value. The deviations in the angles of the carbanionic site C1 are in fact greater. There are small angles between the F and $CF_3$ substituents, but large ones involving the lithium atom, which is the structural consequence of a carbanion-like behavior with a highly polarized Li−C bond (towards C) but also L−F and C−$CF_3$ bonds (towards F and $CF_3$). Large angles in geminal compounds with metal atoms and electronegative non-metal atoms at a common carbon partner are not unusual.[33]

Despite the fact that $LiC_2F_5$ was crystallized from diethyl ether solution, the structure shows its preference for the formation of unexpected Li−F bonds and dimers instead of the alternative solvation of the Li atoms by three ether molecules. To rationalize this fact, we carried out quantum-chemical investigations on the energetics of the formation of

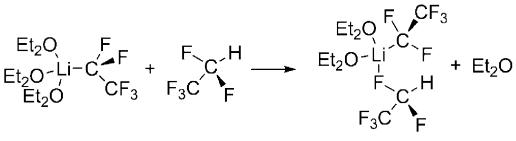


*Scheme 3.* Formation of a dimeric structure from two monomeric molecules under liberation of two solvent molecules.

the solvated dimer from two equivalents of a triple-solvate under loss of two molecules of diethyl ether (Scheme 3).

Preliminary calculations (PBE0/6-31G(d,p)) showed that neither the application of solvent models nor the correction for basis set superposition errors (BSSE; details see Table S7) nor the inclusion of diffuse functions led to significantly different results. The following data result from single-molecule calculations using the (PBE0/6-31G+(d,p)) approximation. They show a clear preference for the dimer with a gain of free energy $\Delta G_{298} = -20.3\ \mathrm{kcal\,mol^{-1}}$. This means that the α-fluorine atoms in $[C_2F_5Li(OEt_2)_2]_2$ are better donors than the ether molecules, possibly because they receive a large negative partial charge as a result of the presence of the adjacent carbanion. This situation is consistent with the expected behavior of a Li/F carbenoid.

The gain of free energy by replacement of a single ether molecule by $C_2F_5H$ without dimerization (Scheme 4) can in the same way be estimated to be $\Delta G_{298} = -3.0\ \mathrm{kcal\,mol^{-1}}$, which seems surprising in the sense that $C_2F_5H$ appears to be a better donor to the $LiC_2F_5(OEt_2)_2$ fragment than $Et_2O$. This helps to explain the observation of residual $C_2F_5H$ in solutions of $LiC_2F_5$, which is discussed in context of NMR spectroscopy experiments below.



*Scheme 4.* Replacement of one ether ligand in $LiC_2F_5(OEt_2)_3$ by a $C_2F_5H$ ligand.

To shed more light on the nature of the bonding in the species discussed we performed analyses of the topologies of the calculated electron-density distributions according to the QTAIM theory.[34] Table 1 contains a selection of important parameters for key bonds in these species.

*Table 1:* Comparison of parameters of the electron-density topology for selected bonds in $LiC_2F_5\cdot 3\,Et_2O$, dimeric $[LiC_2F_5\cdot 2\,Et_2O]_2$, and $LiC_2F_5\cdot 2\,Et_2O\cdot C_2F_5H$ in the calculated ground state (PBE0/6-31+G-(d,p)).[a]

| Bond | Species | $r$ | $\rho$(bcp) | $-\nabla^2\rho$(bcp) |
|---|---|---|---|---|
| Li-C | $LiC_2F_5\cdot 3\,Et_2O$ | 2.152 | 0.20 | −3.25 |
| | $[LiC_2F_5\cdot 2\,Et_2O]_2$ | 2.168 | 0.19 | −3.13 |
| | $LiC_2F_5\cdot 2\,Et_2O\cdot C_2F_5H$ | 2.123 | 0.22 | −3.52 |
| Li-O | $LiC_2F_5\cdot 3\,Et_2O$ | 2.058 | 0.14 | −3.21 |
| | $[LiC_2F_5\cdot 2\,Et_2O]_2$ | 2.022 | 0.15 | −3.54 |
| | $LiC_2F_5\cdot 2\,Et_2O\cdot C_2F_5H$ | 1.971 | 0.17 | −4.22 |
| Li-F | $[LiC_2F_5\cdot 2\,Et_2O]_2$ | 1.945 | 0.15 | −4.00 |
| | $LiC_2F_5\cdot 2\,Et_2O\cdot C_2F_5H$ | 2.264 | 0.06 | −1.54 |

[a] $r$ internuclear distance [Å], electron densities $\rho$(bcp) [$e\,\mathrm{Å}^{-3}$] and Laplacians $-\nabla^2\rho$(bcp) [$e\,\mathrm{Å}^{-5}$] at the bond critical points.

The values show that all bonds to lithium are clearly of ionic nature: negative Laplacians and low electron densities at the bond critical points (bcp; compare values calculated at the same level of theory: C–C(Li) in $LiC_2F_5\cdot 2\,Et_2O\cdot C_2F_5H$: $\rho(\mathrm{bcp}) = 1.85\ e\,\mathrm{Å}^{-3}$, $-\nabla^2\rho(\mathrm{bcp}) = 18.2\ e\,\mathrm{Å}^{-5}$; Li–F molecule $\rho(\mathrm{bcp}) = 0.47\ e\,\mathrm{Å}^{-3}$, $-\nabla^2\rho(\mathrm{bcp}) = -1.69\ e\,\mathrm{Å}^{-5}$). As expected, the Li–C bonds show the highest densities at the bcps, all the Li–O bonds to ether molecules are of comparable nature, but the Li–F bonds are rather different. The one in the solvate $LiC_2F_5\cdot 2\,Et_2O\cdot C_2F_5H$ with a neutral $C_2F_5H$ molecule bonded to an ether solvate of $LiC_2F_5$ features less than half the electron density at the bcp than the Li–F bonds in the dimer $[LiC_2F_5\cdot 2\,Et_2O]_2$: as a consequence of the carbanionic nature of the $LiC_2F_5$ unit, its α-fluorine atom involved in the Li–F interaction is more negatively charged and thus a better donor.

A further interesting aspect of these QTAIM studies was the finding of an atomic interaction line between the F atoms of coordinating $C_2F_5H$ and the carbanionic site in $LiC_2F_5\cdot 2\,Et_2O\cdot C_2F_5H$ (see Figure 2). This is caused by the presence of two electron-rich atoms (F and carbanion) and one electron-poor atom (Li) in close proximity. The contribution of density from the lithium atom is low enough to allow the electron-rich atoms to dominate the situation in the overlap region leading to an F···C atomic interaction line (of low $\rho(\mathrm{bcp}) = 0.05\ e\,\mathrm{Å}^{-3}$, $-\nabla^2\rho(\mathrm{bcp}) = -0.57\ e\,\mathrm{Å}^{-5}$). In some

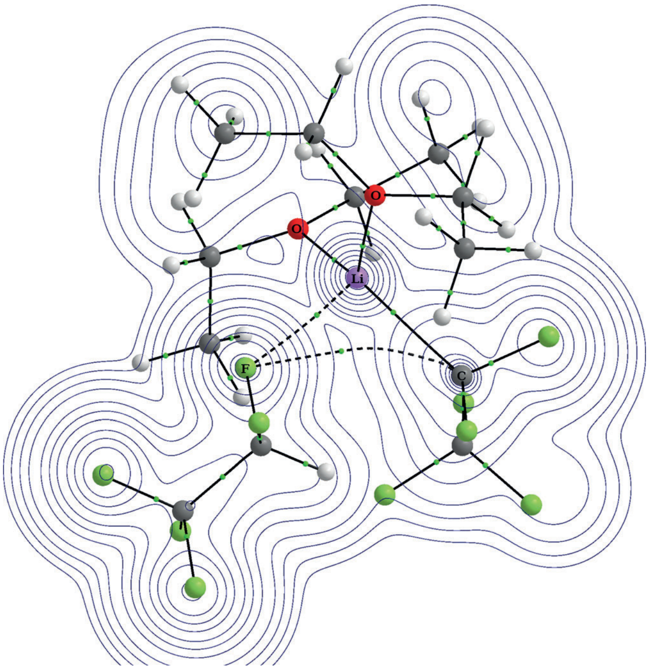


*Figure 2.* Electron-density plot and molecular graph of $LiC_2F_5\cdot 2\,Et_2O\cdot C_2F_5H$ in the plane $LiC_{\mathrm{carbanion}}F_{C_2F_5H}$ (PBE0/6-31+G(d,p)). Peripheral weak interactions have been omitted for clarity.

sense this represents the reverse situation to the absence of atomic interaction lines for weak dative bonds in three-membered rings[35] when an electron-rich atom comes close to this bond, for example, in $F_3SiONMe_2$[19] and $(F_3C)_2BCH_2NMe_2$.[20b]

With the information from the solid state and on the single molecule, we turned to investigate the aggregation behavior of $LiC_2F_5$ in diethyl ether solution and carried out NMR spectroscopy experiments in the temperature range between −90 °C and −30 °C. Surprisingly, even under very careful stoichiometric preparation conditions with a $C_2F_5H$:*n*BuLi ratio of 1:1, signals of $C_2F_5H$ can be observed at low temperatures. This result indicates the system to be a chemical equilibrium. $^{19}F$ and $^{13}C$ NMR spectra have been described elsewhere[36] and were reproduced. The $^{19}F$ NMR spectrum shows two resonances belonging to the $CF_3$ and $CF_2$ groups at −87 and −128 ppm. This data is in seeming contrast to the solid-state structure, as the two fluorine atoms of the $CF_2$ units are chemically different (bridging to Li or terminal); note that the same spectrum was observed over the whole temperature range up to −40 °C at which decomposition starts to occur. No signals of $LiC_2F_5$ remain detectable above −30 °C. Instead the resonance of $C_2F_4$ shows it to be the major fluorine-containing product in solution (besides traces of other compounds with resonances between −70 and −85 ppm). Taking the above results of the calculations into consideration, we conclude the structure in solution to be related to the one in the solid state, yet with a fast exchange in the coordination of the lithium ion by the two α-fluorine atoms. An alternative explanation would be a symmetrical bridging of both α-fluorine atoms, eventually by replacing one ether molecule at each lithium atom. No sign of a decoalescence of the $^{19}F$ resonances has been found in the temperature range to −90 °C.

The $^{13}C\{^{19}F\}$ NMR spectrum and a $^{19}F/^{13}C$ correlated spectrum of $LiC_2F_5$ recorded at −45 °C contain two resonances at 158 ($CF_2$ group) and 126 ppm ($CF_3$ group). Despite $^{19}F$ decoupling both resonances are broad and no coupling pattern to $^{6/7}Li$ can be observed. $^7Li$ NMR spectra of $LiC_2F_5$ in diethyl ether solution contain a single broad signal at 0.2 ppm. Probably because of this line width a coupling between lithium and fluorine nuclei, as observed in loosely related Si-F···Li systems,[37] could not be observed in the present case. The surprising observation of a cross peak between the proton of (residual) $C_2F_5H$ with the lithium atom of product $LiC_2F_5$ in correlated $^7Li/^1H$ NMR spectra indicates again a dynamic process in solution, in which residual $C_2F_5H$ dynamically replaces a solvent molecule, when a small excess of $C_2F_5H$ is present. This finding was reproduced at different field strengths and with different samples.

In conclusion, we demonstrated the isolation of a lithium/fluorine carbenoid and its structure determination in the solid state. As expected, we find long Li−C and C−F bonds at the carbanionic site, but unexpectedly we find that a dimerization under formation of strong Li−F bonds is favored to a complete solvation of the lithium atom in ethereal solution. Calculations and NMR spectroscopy data suggest a dynamic situation in solution, probably with a dimeric structure and also exchange between $[(Et_2O)_2LiC_2F_5]_2$ and free $C_2F_5H$. The observation that 1:1 mixtures of $C_2F_5H$:*n*BuLi contain $C_2F_5H$ suggest an equilibrium process in the formation of $LiC_2F_5$. Now, that the first solid-state structure of a Li/F carbenoid has been elucidated, we are optimistic that further research will contribute to a general understanding of the structure—reactivity relationship of this highly interesting and very useful class of molecules.

Received: June 25, 2014
Revised: July 24, 2014
Published online: September 9, 2014

**Keywords:** aggregation · carbenoid · crystal structure · fluorine · lithium

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[27] $C_{20}H_{40}Li_2O_4F_{10}$, $M_r = 548.40$, crystal size $0.29 \times 0.28 \times 0.25$ mm$^3$, monoclinic space group $P2_1/n$, $a = 11.5923(10)$ Å, $b = 10.5964(8)$ Å, $c = 11.6103(11)$ Å, $\beta = 94.559(8)°$, $V = 1421.7(2)$ Å$^3$, $T = 100.0(1)$ K, $Z = 2$, $\rho_{calcd} = 1.281$ g cm$^{-3}$, $\mu(Mo_{K\alpha}) = 0.127$ mm$^{-1}$, radiation used $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), $2\theta_{max} = 50°$, 10179 reflections measured, 2491 unique, $R_{int} = 0.0539$, completeness 99.0%. The final $wR2$ was 0.1317 for all data and $R1$ was 0.0461 for 1905 reflections with $I > 2\sigma(I)$. Using Olex2 [O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339 – 341], the structure was solved using Direct Methods and refined using Least Squares minimization with the ShelX program package [G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112 – 122]. CCDC 1001406 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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