neutral alumina (3 mL, activity 2–3) and eluted with diethyl ether (~14 mL). Evaporation of the solvent gave the product. Yields were determined by ^{1}H NMR integration against a known amount of 1,2-dibromoethane. The immobilized catalyst was reused as such in further experiments.

Determination of catalyst leaching: A 100 mL Schlenk flask was charged with FRPSG supported catalyst (500 mg, 10 mg Pd complex per g FRPSG, 1.48 μmol), 4-bromonitrobenzene (303 mg, 1.50 mmol), and phenylboronic acid (205 mg, 1.68 mmol), evacuated and refilled with argon (3×). DME (10 mL) and Na_2CO_3 (2 M in water, 5.0 mL, 10.0 mmol) were added. The flask was shaken under argon at 80 °C for 15 h, and then the reaction mixture was cooled to room temperature and filtered. The residue was washed with DME (2×10 mL), water (2×10 mL), and again with DME (2×10 mL), and the organic and aqueous filtrates were collected separately. The solvents were removed in vacuo, the resulting solids were powdered, and the Pd content determined by ICP-MS.

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9,9-Dilithiofluorene: The First Crystal-Structure Analysis of an α,α-Dilithiated Hydrocarbon**

Gerald Linti,* Alexander Rodig, and Hans Pritzkow

Lithiated hydrocarbons are one of the most important classes of compounds in organoelement chemistry. Many of these compounds have been structurally investigated in solution and the crystalline state, as well;[1–3] di- and oligometallated species earned special interest.[4,5] Dilithiomethane is mentioned as one example here, it is available from the thermolysis of lithium methanide[6,7] and used in many synthetic procedures. A series of oligomeric structures of lithium methanide was investigated with quantum-chemical methods, in which carbon atoms take the coordination number six.[8] In monomeric dilithiomethane the planar coordination of the carbon atom is only less stable than the tetrahedral coordination of the carbon atom by 71 kJ mol^{-1}.[9,10] However, the final structure in solution and of the solid state has not been determined.[11,12] Several substituted derivatives, such as Me_3CCHLi_2, $Me_3SiCHLi_2$,[13] and the title compound 9,9-Dilithiofluorene,[14] have been synthesized, but their structures are not known. It was possible to solve the crystal structures of heteroatom substituted derivatives, such as $PhS(O)(NMe)CLi_2Ph$,[15] $(Me_3SiNPPh_2)_2CLi_2$,[16,17] $(MeO)_2P(O)CLi_2SiMe_3$ (as aggregate with dimethylamide),[18] and $PhSO_2CLi_2(SiMe_3)$,[19] where Li–O and Li–N bonds dominate the structures. The anion $(CHPMe_2NSiMe_3)^{2-}$ together with $BuMe_2SiO^-$ forms the backbone of a Li_{14} cluster.[20] $[\{(Me_3Si)_2CH\}_6Al_2CH_2Li_2]$ was considered as a R_3Al-adduct to CH_2Li_2.[21] Herein, we describe the crystal structure of the 9,9-dilithiofluorene complex **2** [Eq. (1)].

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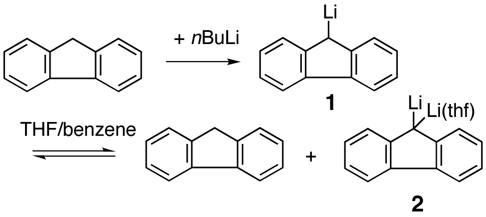
If lithiofluorene **1** is dissolved in a solvent mixture of benzene:THF (10:1) at 0 °C pale orange cubes of **2** crystallize [Eq. (1)]. On redissolving of crystallized **2** in THF or benzene, in the ^{1}H and ^{13}C NMR spectra only the resonance signals of **1** can be observed. Therefore, it was not possible to investigate **2** in solution. Donor-free $Li_2C_{13}H_8$ has already been prepared by the thermolysis of lithiofluorene and its constitution demonstrated by deuterolysis experiments.[14]



(1)

Compound **2** crystallizes together with one molecule of benzene in the orthorhombic crystal system (space group *Pnma*).[22] In the crystal structure the fluorenylidene units are each linked together by two lithium atoms to form polymeric chains (Figure 1). These can be considered as a double ribbon of lithium atoms, which are bridged alternately by fluorenylidene groups and THF molecules, that is, a planar band of edge-connected Li_2C_2 and Li_2CO rings results. The Li–Li separations within the rings ($d_{Li-Li} = 264.9(4)–268.0(4)$ pm) are similar to those in aggregated lithium alkanides $(LiR)_n$ (R = Me, Et, Bu).[23–25] Markedly longer ($d_{Li-Li} = 427$ pm) are the fluorene-bridged Li–Li separations. The lithium cations coordinate to both sides of the five-membered ring of the fluorene groups. Here, the coordination of Li1 ($d_{Li-C} = 222.9$, 242.3, 245.3, 279.5, and 285.6 pm) may be considered as η^3, that of Li2 ($d_{Li-C} = 234.3–256.7$ pm) as η^5. Both of the lithium atoms are shifted from the center of the ring towards C9. In the $[Cp_2Li]^-$ ion ($Cp = C_5H_5$) the lithium atom is positioned almost between the centers of the rings and the Li–C separations are in a narrower range ($d_{Li-C} = 229.8(4)–236.2(3)$ pm).[26] In addition, every lithium atom has an interaction with the carbon atom C9 of a second fluorenylidene ring on the other side of the ribbon ($d_{Li-C} = 216.1$, 218.6 pm) and a Li–O bond. The THF molecules coordinate in a bridging mode between two lithium atoms. The distances between the oxygen atom and the lithium centers are in the normal range ($d_{Li-O} = 198.3(3)–205.7(3)$ pm).[1]

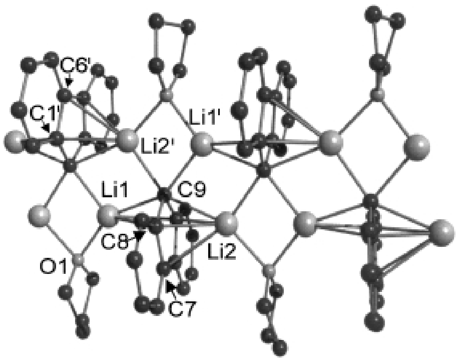


Figure 1. Section of the polymeric structure of **2** (hydrogen atoms are omitted for clarity). Selected bond lengths [pm] and angles [°]: C9-Li1 222.9(3), C9-Li1′ 216.1(13), C9-Li2′ 218.6(3), C9-Li2 234.3(3), C1-Li1 242(1), C1-Li2, 237(1), C6-Li2 257(2), C7-Li2 253(1), C8-Li1 245(2), C10-Li2 241(2), Li1-O1 197.8(3), Li2-O1 205.4(3), C1-C9 147.4(7), C8-C9 141.0(8), C1-C6 145.2(9), C6-C7 141.7(6), C7-C8 144.5(9) Li1-Li2′ 267.5(4), Li1-Li2′ 265.3(4); Li1-C9-Li2 75.9(1), C1-C9-C8 102.3(3). C1 and C6 are not labeled, however, they are symmetry equivalents of C1′ and C6′.

The atom C9 is coordinated by four lithium ions; the corresponding lithium–carbon separations are the shortest found in **2** ($d_{Li-C} = 215.9(13)$, 219.1(3), 222.4(3), and 234.2(3) pm). On the whole, C9 is sixfold coordinate. Usually, this coordination number is only found for carbon in clusters such as $[\{C(AuPPh_3)_6\}]^{2+}$.[27,28] In quantum-chemically calculated structures of $(CH_2Li_2)_2$ as well as in $[(Me_3Si)_2CH]_6Al_2$-CH_2Li_2,[29], short Li–C bonds lead to a coordination number of six for the carbon atoms. A comparison of the lithium–carbon bonds of the six coordinated carbon atoms in $(CH_2Li_2)_2$ ($d_{Li-C} = 195.5$ pm and 239.7 pm; Figure 2) and **2** reveals, at least regarding these distances, good agreement of the calculated model with the experimental data for **2**.

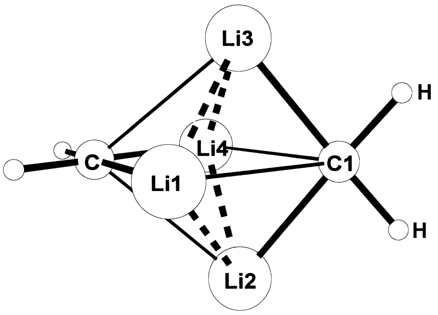


Figure 2. Calculated structure of $(CH_2Li_2)_2$ from ref. [29]. Selected bond lengths [pm] and angles [°]: Li1-Li2 223.4, Li1-Li4 303.4, Li1-C1 239.7, Li2-C1 195.5; H-C1-H 97.76, Li4-C1-Li1 101.79.

To get a better insight into the bonding and structural situation of this class of compounds, density functional calculations on a model compound by using an uniform SV(P) base set for all atoms were performed (B-P86 functional).[30–35] As a model system, which is treatable by quantum-chemical methods, **3**, which exhibits only a section of the polymeric structure of **2** was used. This section consists of two fluorenylidene fragments, six lithium atoms, and six water molecules (which replace THF). Thus, **3** is a doubly positive charged $[Li_6(C_{13}H_8)_2(H_2O)_6]^{2+}$ ion. The basic structural motif of **2** remains nearly unchanged (Figure 3). This conformity is also found with the corresponding bond lengths and angles. Deviations in the structure of **2** compared to **3** can be derived from the enormous shortening of the original polymeric molecule chain in **2** to the "molecule chain" in **3**, which contains only two fluorenylidene units.

In addition, the shared electron numbers (SEN), obtained by Ahlrichs–Heinzmann population analyses,[36] confirm, that there are no significant lithium–lithium interactions in **3** ($SEN_{Li-Li} < 0.1$). It is found, too, that in **3** the negative partial charges are located mainly at the carbon centers C9 and C22 ($\delta_{C9,C22} = -0.5$, $\delta_{Li} = +0.5$).

The structures of **2** and **3** differ markedly from that of **1**, which forms a sandwich-type dimer, where the lithium ions

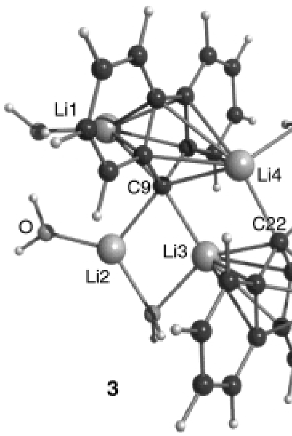


Figure 3. View of the calculated structure of **3**. Selected lithium–carbon bond lengths and the lithium–lithium separations [pm] of **3**: Li1-C9 228.8, Li2-C9 219.4, Li3-C9 220.3, Li4-C9 234.3, Li3-C22 222.3, Li4-C22 220.0, Li5-C22 214.7, Li6-C22 228.7, Li1-$C_{fluorene}$ 227.6–239.5, Li3-$C_{fluorene}$ 220.3–276.5, Li4-$C_{fluorene}$ 234.3–273.7, Li6-$C_{fluorene}$ 228.7–249.7, Li2-Li3 260.4, Li3-Li4 271.5, Li4-Li5 269.7, Li5-Li6 292.6.

are coordinated by the six-membered rings.[37] For **1**, a polymeric array with coordination of the five-membered rings is calculated to be less stable by 112 kJ mol^{-1}. Such a structure would correspond to the structures of CpLi,[38] $[Cp_2Li]^-$,[26] and $[Cp^B_2]^-$[39] ($Cp^B = (C_6H_5CH_2)_5C_5$). In fluorenyl lithium bis(quinuclidin) the lithium atom is bonded to C1, C2, and C9 in a η^3-mode.[40] Comparing two monomeric dilithiofluorene molecules **4** and **5**, which have a lithium atom bonded terminal to C9 as well as a second one, bonded to the five- or six-membered ring respectively, the structure of **5** is calculated to be more stable by 30 kJ mol^{-1} (Figure 4). In **4** the negative charge is located mainly at C9, as is the case in **3**. In contrast, in **5**, C9 and C8 ($\delta = -0.32$) as well as C1 and C12 ($\delta = -0.13$, -0.19) have high negative partial charges.

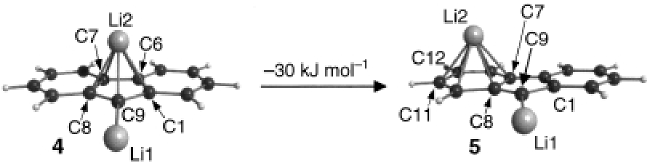


Figure 4. View of the calculated structures of **4** and **5**. Lithium–carbon bond lengths [pm]: **4**: Li1-C9 198.6, Li2-C9 214.9, Li2-C1 216.7, Li2-C8 216.7, Li2-C6 224.6, Li2-C7 224.5; **5**: Li1-C9 198.6, Li2-C 223.9–226.3.

The observed structure of **2** is remarkable for several reasons. In this X-ray structurally characterized dilithiated hydrocarbon an unsymmetrical η^5 coordination of the fluorene group is present. Therefore, **2** contains a carbon atom, which is six-coordinate, being bound to four lithium and two carbon atoms. Thus, Li_2C_5-sandwich-columns are formed (the inverse of Cp_2Li-type sandwich compounds), which are linked by additional σ-Li–C interactions to form ribbons.

Experimental Section

Freshly prepared **1** (0.9 g, 4.9 mmol) was dissolved in a mixture of benzene (50 mL) and THF (5 mL). The solution was filtered and reduced to a volume of 15 mL. On cooling to 0 °C; **2** (0.26 g, 18 % based on **1**) crystallized as orange crystal cubes.

^{1}H NMR (250 MHz, C_6D_6, 25 °C, TMS): $\delta = 1.16$ (cm, thf), 3.17 (cm, thf), 5.78 (s, $LiC_{13}H_9$), 6.86–7.16 (m, $LiC_{13}H_9$), 7.34 (t, $LiC_{13}H_9$), 7.70 (d, $LiC_{13}H_9$), 8.20 ppm (d, $LiC_{13}H_9$); ^{13}C NMR (C_6D_6, 25 °C, TMS): $\delta = 25.1$ (thf), 68.3 (thf), 74.8 ($LiC_{13}H_9$), 113.1 ($LiC_{13}H_9$), 118.2 ($LiC_{13}H_9$), 120.2 ($LiC_{13}H_9$), 121.6 ($LiC_{13}H_9$), 122.5 ($LiC_{13}H_9$), 134.8 ppm ($LiC_{13}H_9$).

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