$[Li_4(CH_2NMe_2)_4(THF)_4]$: An Unusual Tetrameric but Not Tetrahedral σ-Organolithium Compound†

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Summary: Recrystallization of unsolvated $LiCH_2NMe_2$ *(**1**) from n-hexane/THF/diethyl ether gave* $[Li_4(CH_2NMe_2)_4(THF)_4]$ *(**2**), which lost THF easily in vacuo to regenerate compound **1**. In the solid state, **2** is tetrameric (*C_i *symmetry). There are two different (N,N-dimethylamino)methyl ligands with a 1,2κC:3κN and 1,3κC:1κN coordination, respectively. Two lithium centers are pentacoordinated by Li, N and three C atoms, and the other two adopt tetrahedral coordination defined by C, N, and two O atoms. The structure of **2** can be understood as that of an opened* Li_4 *tetrahedron.*

Introduction

Starting with the investigations on Köbrich's carbenoids, $LiCH_2X$ (X = Cl, Br),[1] many organolithium compounds of type $LiCH_2YR_n$ (R = alkyl, aryl) with Lewis-basic heteroatom centers Y (Y = N, P, O, S, X) were prepared and characterized. All of these compounds, with chelating *N,N′*-coligands, that have been structurally characterized thus far have been dimers, either with six-membered $Li_2C_2Y_2$ rings in which the heteroatoms Y are coordinated to lithium ($[Li_2(CH_2YR_n)_2(NN)_2]$ (YR_n = SPh, PPh_2, PMe_2, PPhMe; NN = TMEDA, sparteine)[2−5] or with four-membered Li_2C_2 rings without coordination of Y to lithium ($[Li_2(CH_2SMe)_2(TMEDA)_2]$)[2].

Very recently, we reported the first examples of the solid-state structures of such lithium compounds which did not contain chelating *N,N′*-ligands. $[\{Li(CH_2YR_n)(THF)\}_\infty]$ (YR_n = SMe, PPh_2)[6,7] had polymeric ladder-like structures, and $[Li_2(CH_2YR_n)_2(THF)_x]$ (YR_n = SPh, $x = 4$; $YR_n = NPh_2$, $x = 3$)[6,8] were dimers with central four-membered Li_2C_2 rings. Also structurally characterized was the tetrameric complex $[Li_4(CH_2NC_5H_{10})_4(THF)_2]$ (**3**, NC_5H_{10} = piperidino)[8] containing a characteristic Li_4 tetrahedron.

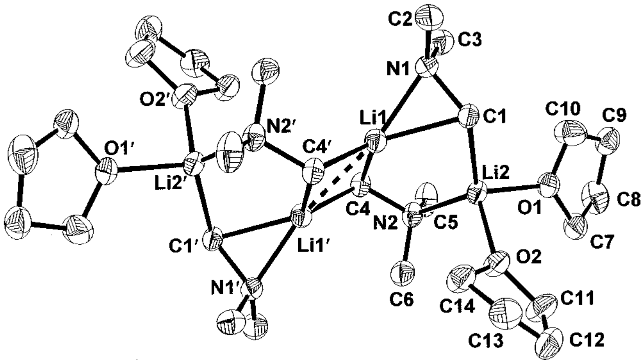

Figure 1. ORTEP[10] drawing of the molecular structure of **2** (thermal ellipsoids at 30% probability). Hydrogen atoms are omitted for clarity.

We report here a single-crystal X-ray diffraction analysis of $[Li_4(CH_2NMe_2)_4(THF)_4]$ (**2**), which exhibits a new structural feature in organolithium chemistry.

Results and Discussion

The transmetalation between $Bu_3SnCH_2NMe_2$ and BuLi in *n*-hexane afforded pyrophoric unsolvated (*N,N*-dimethylamino)methyllithium, $LiCH_2NMe_2$ (**1**), as a colorless powder in nearly quantitative yield.[8,9] At −78 °C, recrystallization of **1** from *n*-hexane/THF/diethyl ether gave well-shaped crystals of $[Li_4(CH_2NMe_2)_4(THF)_4]$ (**2**), which were suitable for single-crystal X-ray analysis. These could not be separated from the mother liquor and properly dried because the THF solvate molecules were rapidly lost under argon and in vacuo to regenerate colorless microcrystals of **1**. The low stability of crystalline **2** indicates a very weak coordination of THF. In contrast, the THF molecules in the dimeric complex $[Li_2(CH_2NPh_2)_2(THF)_3]$ are more strongly coordinated and are not lost in vacuo.[8]

The ORTEP[10] representation of the molecular structure of **2** is shown in Figure 1. Selected distances and bond angles are listed in Table 1. Compound **2** forms tetrameric molecules (C_i symmetry) with a planar four-membered Li_2C_2 ring whose midpoint is the inversion center. Two of the four (dimethylamino)methyl ligands (C4, N2, C5, C6) are arranged in a 1,2*κC*:3*κN* fashion, whereas the other two (C1, N1, C2, C3) exhibit a 1,3*κC*:1*κN* coordination mode.

Ignoring a weak Li1···Li2 interaction (d(Li1···Li2) = 2.785(5) Å), Li1 is pentacoordinated by one Li, one N,

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† Dedicated to Prof. Heinrich Nöth on the occasion of his 70th birthday.

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Table 1. Selected Distances (Å) and Angles (deg) for $[Li_4(CH_2NMe_2)_4(THF)_4]$ (2)

Li1−C1	2.145(4)	Li1−C4′	2.207(4)
Li1−C4	2.228(4)	Li2−C1	2.192(4)
Li2−C4	2.854(4)	Li1−Li1′	2.409(6)
Li1−Li2	2.785(5)	Li1−N1	2.044(3)
Li2−N2	2.107(3)	Li2−O1	2.017(3)
Li2−O2	2.032(3)	N1−C1	1.490(3)
N1−C2	1.464(3)	N1−C3	1.443(3)
N2−C4	1.497(3)	N2−C5	1.461(3)
N2−C6	1.445(3)		

Li1−C4−Li1′	65.8(1)	C4−Li1−C4′	114.2(1)
Li2−Li1−Li1′	103.2(2)	Li1−C1−N1	65.6(1)
C1−Li1−N1	41.6(1)	Li1−C1−Li2	79.9(1)
Li1−C4−N2	110.8(1)	C1−Li1−C4	113.9(2)
C1−Li1−C4′	122.2(2)	N1−Li1−C4′	123.8(2)
C1−Li2−N2	121.9(2)	Li2−N2−C4	103.4(1)
O1−Li2−O2	101.4(1)	O1−Li2−N2	106.8(2)
O2−Li2−N2	108.5(2)	O1−Li2−C1	109.8(2)
O2−Li2−C1	106.7(2)		

[a] Symmetry transformation used to generate equivalent atoms: ′ = −x, −y, −z + 1.

and three C atoms. The Li1−C4 and Li1−C4′ bond lengths (2.228(4), 2.207(4) Å) are comparable with those in the Li_2C_2 ring of $[Li_2(CH_2NPh_2)_2(THF)_3]$ (2.246(9), 2.235(9) Å)[8] in which one Li is also five-coordinate. The Li1···Li1′ distance of 2.409(6) Å is typical for organolithium compounds containing an Li_2C_2 ring.[11] Furthermore, Li1 shows very close contacts to C1 (*d*(Li1−C1) = 2.145(4) Å) and N1 (*d*(Li1−N1) = 2.044(3) Å), forming a lithiaazacyclopropane ring. Li1 also is part of a five-membered Li_2C_2N ring that is arranged in approximately an envelope-conformation with C1 being 0.731(4) Å out of the least-squares plane (Li1, Li2, N2, C4).

Li2 is coordinated in a distorted tetrahedron by one methylene carbon atom (*d*(Li2−C1) = 2.192(4) Å), two oxygen atoms of the THF molecules (*d*(Li2−O1) = 2.017(3) Å; *d*(Li2−O2) = 2.032(3) Å), and one nitrogen atom of the bridging aminomethyl ligand (*d*(Li2−N2) = 2.107(3) Å). The Li−N bond lengths in **2** are in line with values found for $[Li_4(CH_2NC_5H_{10})_4(THF)_2]$ (**3**, 2.04(2), 2.06(2) Å)[8] and for lithium amides, e.g., $[\{[LiN(CH_2Ph)_2]_2(dioxane)\}_\infty]$ (1.939(7)−2.037(7) Å),[12] and $[\{Li[N(CH_2Ph)]_2\}_3]$ (1.907(8)-2.038(5) Å).[13] The Li2−C4 distance of 2.854(4) Å indicates only a very weak interaction if any.

A striking feature of the structure of **2** is the lithiaazacyclopropane ring (Li1C1N1) that exhibits the shortest Li−C bond in **2**. Quantum chemical calculations of $LiCH_2NH_2$ revealed[14] that in the most stable monomeric isomer (formula **A**, values in angstroms), lithium also bridges the anionic carbon and the nitrogen atom, whereas the most stable dimer (formula **B**, Δ*E*(**A**/**B**) = 58 kcal/mol in favor of **B**) forms a six-membered $Li_2C_2N_2$ ring. The Li1−C1 bond in **2** (2.145(4) Å) is between the calculated Li−C bond lengths of **A** (1.929 Å) and **B** (2.272 Å).

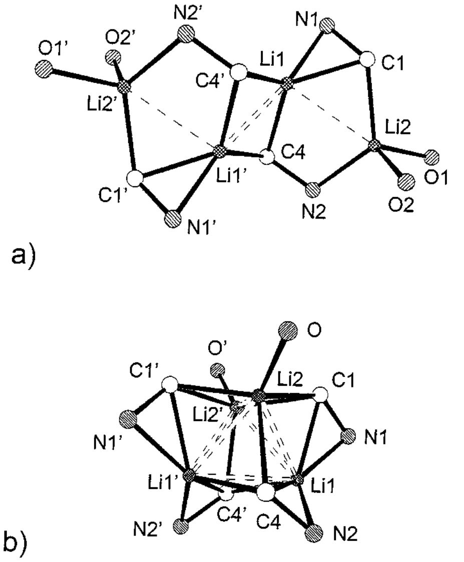
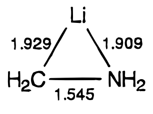
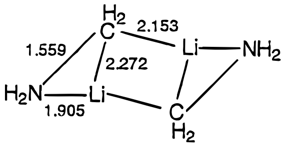


Figure 2. Structure motif of the complexes (a) $[Li_4(CH_2NMe_2)_4(THF)_4]$ (**2**) and (b) $[Li_4(CH_2NC_5H_{10})_4(THF)_2]$ (**3**).[8] The numbering in b corresponds to that in a.



A



B

The structure of **2** can be understood as that of an opened Li_4 tetrahedron; see Figure 2a. To close it, at least two of the four THF molecules must be lost and Li2/Li2′ must approach to form the bonds C1′−Li2/C1−Li2′ and C4−Li2/C4′−Li2′. To obtain the same structure as that of the tetrahedral (piperidino)methyl complex **3**[8] (see Figure 2b), the N2-coordination must be rearranged from Li2 to Li1.

The vast majority of tetranuclear organolithium species exhibits a tetrahedral arrangement of lithium atoms.[11] Only few nontetrahedral Li_4 arrangements are known, all of which are stabilized by strong π-bonds between lithium and the organo ligand.[15] Thus, the structure motif of **2** is unique in σ-organolithium chemistry.

Experimental Section

General Comments. All reactions and manipulations were carried out under purified argon using standard Schlenk techniques. *n*-Hexane was dried with $LiAlH_4$. Diethyl ether and THF were distilled from sodium benzophenone ketyl. A 15% solution of BuLi in hexane (Merck) was used as received. $Bu_3SnCH_2NMe_2$ and $LiCH_2NMe_2$ (**1**) were prepared according to published procedures.[8,9,16] **(Warning: compound 1 as a solid is pyrophoric. Appropriate precautions should be taken for its safe manipulation.)**

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Table 2. Crystal Data and Structure Refinement for Compound 2

empirical formula	$C_{28}H_{64}Li_4N_4O_4$
fw	548.59
T (K)	213.1(2)
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a (Å)	9.566(3)
b (Å)	9.991(4)
c (Å)	10.626(4)
α (deg)	75.50(4)
β (deg)	68.17(4)
γ (deg)	80.82(4)
V (Å^3)	910.2(6)
z	1
D_{calcd} (g cm^{-3})	1.001
μ(Mo Kα) (mm^{-1})	0.064
F(000)	304
scan range (deg)	$2.11 < \theta < 24.00$
no. of reflns colld	9219
no. of indep reflns	2692
no. of params refined	301
goodness-of-fit on F^2	1.037
R_1 [$I > 2\sigma(I)$]	0.0587
wR_2, all data	0.1525
largest diff peak and hole (e Å^{-3})	0.208 and −0.230

X-ray Structure Determination of 2. Suitable colorless single crystals of **2** were obtained by slow cooling a *n*-hexane/THF/diethyl ether (20:1:1) solution of $LiCH_2NMe_2$ (**1**) from ambient temperature to −78 °C. Because of the instability of **2**, crystals were taken directly from the cooled solution (−78 °C) and selected under cold pefluoro ether. A suitable crystal was quickly mounted on a glass fiber under a cold stream of dry nitrogen and measured on a Stoe IPDS diffractometer with Mo Kα radiation (0.710 73 Å, graphite monochromator). A summary of crystallographic data, details of data collection, structure solution, and refinement is given in Table 2. The structure was solved by direct methods with SHELXS-86[17] and refined using full-matrix least-squares procedures on F^2 (SHELXL-93[18]). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included with isotropic thermal parameters of 1.2 times the equivalent isotropic thermal parameters of the corresponding carbon atoms.

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Supporting Information Available: Complete tables of atomic coordinates, H atom parameters, bond distances, bond angles, and anisotropic thermal parameters (6 pages). Ordering information is given on any current masthead page.

OM971020L

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