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STRUCTURE OF THE SIMPLE LITHIUM CHELATE $(LiCH_2CH_2CH_2NMe_2)_4$

KEN S. LEE, PAUL G. WILLIARD* and J. WILLIAM SUGGS*
Department of Chemistry, Brown University, Providence, Rhode Island 02912 (U.S.A.)

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Summary

The structure of $(LiCH_2CH_2CH_2NMe_2)_4$ was determined by single-crystal X-ray difffraction at −100°C. The crystal was monoclinic, space group $P2/n$, a 9.659(2), b 7.007(1), c 18.896(5) Å, β 97.61 (2)°. The structure consisted of a tetrahedron of lithium atoms with each face bridged by carbon. The conformation of the five-membered lithium chelate ring was essentially the same as that found for a palladium chelate of the same ligand.

Introduction

The structures of organolithium reagents have been receiving increasing attention, from both experimental and theoretical directions [1]. This interest arises from the novel structures found (and predicted) for organolithium compounds and from the importance of organolithium reagents to organic synthesis. Many synthetic organic chemists can provide anecdotal evidence for changes in the reactivity of RLi molecules by small changes in reaction conditions, but the effects of the environment on structure (and reactivity) of organolithium reagents are not yet fully understood.

One class of RLi molecules for which several structural studies have been reported is that of chelated organolithiums. A review of the synthetic applications of such molecules has appeared [2]. Among simple chelates with nitrogen or oxygen donors the molecules 8-(dimethylamino)-1-lithionaphthalene (**1**) [3], 3-lithio-1-methoxybutane (**2**) [4], 1-lithio-2-dimethylaminomethylbenzene (**3**) [5] and (2,6-dimethoxyphenyllithium) lithium oxide (**4**) [6] have been the successful objects of X-ray crystallographic studies. We became interested in the structure of a related molecule, 3-dimethylamino-1-lithiopropane (**5**). This is the parent structure of five-membered ring lithium chelates with a nitrogen donor atom. Its synthesis has been described by Thiele and coworkers, who have gone on to prepare other metal chelates based on this ligand [7,8]. The lithium chelate was reported to exist as a tetramer in benzene and as a monomer in 1,4-dioxane. Of particular interest to us was the conformation of the five-membered ring in **5**, since we previously had synthesized the palladium chelate $[Me_2NCH_2CH_2CH_2PdCl]_2$ (**6**) and determined its

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crystal structure [9]. We wanted to see what effect changing the metal species had on the conformation of the five-membered ring by comparing the structures of **5** and **6**.

Experimental

The lithium chelate was prepared as described by Thiele [7] and crystals were grown from ether. Data collection and analysis were carried out on a Nicolet R3m/E diffractometer system at −100°C. The SHELXTL system of programs was used for data reduction, structure determination, refinement, graphics and tables. The chief crystallographic data are summarized in Table 6. Reflection data were collected with 2θ scans, and three standard reflections were measured at the beginning and after every 100 reflections. The structure was partially solved by direct methods. The nitrogen atom and some of the carbon atoms were found readily, and the rest of the carbon atoms, lithium atom and some of the hydrogen atoms followed from Fourier difference maps. The structure was refined to minimize $\Sigma w(|F_0 - F_c|^2)/\Sigma F_0^2$. Temperature factors of all nonhydrogen atoms were anisotropic. All hydrogen atoms except H(1A), H(1B), H(6A), and H(6B) were inserted in theoretical positions, each with an isotropic temperature factor parameter 20% larger than the equivalent isotropic parameter for the carbon atom to which it is bonded. The hydrogen atoms on C(1) and C(6) were constrained to be isotropic and refined to have a bond length of 0.97 Å to the carbon and to have the e.s.d. of 0.002. A final difference map exhibited no peaks larger than 0.75 eÅ^{-3} and none were in chemically meaningful positions.

Results and discussion

Figure 1 is a plot of the results of the crystallographic structure determination of **5**. The observed atomic coordinates, bond lengths, bond angles, anisotropic temperature factors and summary of intensity collection data are given in Tables 1–6. The molecule is a tetramer, with a distorted tetrahedron of lithium atoms having carbon atoms bridging each tetrahedral face. Another way to describe the core is as a distorted cube, with each face a puckered C_2Li_2 ring. The two halves of the tetramer are related by a two-fold axis. An analogous core is seen for other tetrameric alkyllithiums [10]. The lithium–lithium distances of 2.47 and 2.54 Å are close to the values found for other alkyllithium tetramers.

It is interesting to compare the structure of **5** with the chelates **2** and **3**. The C–Li bond lengths in **3** are 2.25, 2.29 and 2.31 Å to an aromatic carbon. In the case of **5** the distances are 2.24, 2.27 and 2.28 Å to an aliphatic carbon. While one normally finds bonds to aromatic carbons to be shorter than bonds to aliphatic carbons, this is not always the case with organolithium compounds. For example, the average C–Li distance in $(PhLi \cdot OEt_2)_4$ is 2.30 Å [11], while for $(EtLi)_4$ it is 2.27 Å [10]. Comparing the specific case of **3** vs. **5**, the difference is average C–Li distance may reflect the different nature of the chelate rings which are formed. The five-membered ring in **3** has to accommodate a large angle exocyclic to the aromatic ring and at the same time allow the carbon to coordinate to three lithium atoms. The structure adopted by **3** has longer C–Li bonds and a short N–Li distance of 2.01 Å. With the more flexible saturated chelate in **5**, the carbon–lithium distance has shortened and the N–Li distance has increased to 2.06 Å. The structure of **2** and **5** are quite similar.

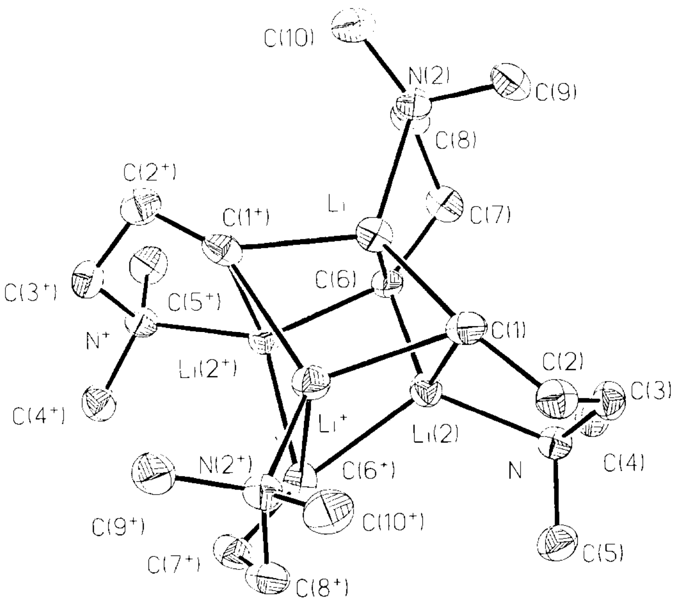

Fig. 1. A plot of the structure of $(LiCH_2CH_2CH_2NMe_2)_4$ showing the atomic numbering.

the chief difference being the average C–Li distance of 2.31 Å for **2**, compared to 2.26 Å for **5**. This is to be expected for bonds to secondary vs. primary carbons.

Previously, we had prepared the palladium chelate **6** from $(PhCN)_2PdCl_2$ and $n\text{-}Bu_3SnCH_2CH_2CH_2NMe_2$ and solved its crystal structure [9]. We wanted to compare the conformations of the five-membered rings in the transition metal and alkali metal complex. Carbons bonded to lithium and to palladium exhibit different reactivities and we wanted to see if there were any corresponding differences in

TABLE 1

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($Å^2 \times 10^3$)

Atom	x	y	z	U [a]
Li(1)	1740(4)	8600(5)	7999(2)	26(1)
Li(2)	3584(4)	11022(5)	7956(2)	25(1)
N(1)	5230(2)	11823(2)	8710(1)	24(1)
N(2)	473(2)	7798(3)	8744(1)	25(1)
C(1)	4055(3)	7866(3)	8135(1)	28(1)
C(2)	5562(3)	8331(3)	8486(1)	31(1)
C(3)	5606(3)	9938(3)	9027(1)	29(1)
C(4)	4875(3)	13151(3)	9260(1)	34(1)
C(5)	6400(3)	12628(4)	8386(1)	35(1)
C(6)	1450(3)	11753(3)	8218(1)	28(1)
C(7)	935(3)	11290(3)	8944(1)	30(1)
C(8)	–120(3)	9669(3)	8896(1)	30(1)
C(9)	1297(3)	7020(4)	9386(1)	34(1)
C(10)	–657(3)	6445(4)	8506(1)	35(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 2

BOND LENGTHS (Å)

Li(1)–Li(2)	2.469(5)	Li(1)–N(2)	2.062(4)
Li(1)–C(1)	2.276(5)	Li(1)–C(6)	2.272(4)
Li(1)–Li(1a)	2.539(8)	Li(1)–Li(2a)	2.467(5)
Li(1)–C(1a)	2.240(4)	Li(2)–N(1)	2.067(4)
Li(2)–C(1)	2.274(4)	Li(2)–C(6)	2.242(5)
Li(2)–Li(1a)	2.467(5)	Li(2)–Li(2a)	2.530(7)
Li(2)–C(6a)	2.273(4)	N(1)–C(3)	1.476(3)
N(1)–C(4)	1.469(3)	N(1)–C(5)	1.468(3)
N(2)–C(8)	1.474(3)	N(2)–C(9)	1.464(3)
N(2)–C(10)	1.471(3)	C(1)–C(2)	1.552(3)
C(1)–Li(1a)	2.240(4)	C(2)–C(3)	1.518(3)
C(6)–C(7)	1.554(3)	C(6)–Li(2a)	2.273(4)
C(7)–C(8)	1.521(3)		

TABLE 3

BOND ANGLES (deg.)

Li(2)–Li(1)–N(2)	134.9(2)	Li(2)–Li(1)–C(1)	57.1(1)
N(2)–Li(1)–C(1)	121.6(2)	Li(2)–Li(1)–C(6)	56.2(1)
N(2)–Li(1)–C(6)	92.4(2)	C(1)–Li(1)–C(6)	110.0(2)
Li(2)–Li(1)–Li(1a)	59.0(1)	N(2)–Li(1)–Li(1a)	164.0(1)
C(1)–Li(1)–Li(1a)	55.1(2)	C(6)–Li(1)–Li(1a)	103.4(1)
Li(2)–Li(1)–Li(2a)	61.7(2)	N(2)–Li(1)–Li(2a)	131.1(2)
C(1)–Li(1)–Li(2a)	105.4(2)	C(6)–Li(1)–Li(2a)	57.1(1)
Li(1a)–Li(1)–Li(2a)	59.1(1)	Li(2)–Li(1)–C(1a)	106.5(2)
N(2)–Li(1)–C(1a)	115.6(2)	C(1)–Li(1)–C(1a)	105.3(2)
C(6)–Li(1)–C(1a)	111.3(2)	Li(1a)–Li(1)–C(1a)	56.5(1)
Li(2a)–Li(1)–C(1a)	57.5(1)	Li(1)–Li(2)–N(1)	131.0(2)
Li(1)–Li(2)–C(1)	57.2(1)	N(1)–Li(2)–C(1)	92.3(2)
Li(1)–Li(2)–C(6)	57.4(1)	N(1)–Li(2)–C(6)	115.5(2)
C(1)–Li(2)–C(6)	111.2(2)	Li(1)–Li(2)–Li(1a)	61.9(2)
N(1)–Li(2)–Li(1a)	134.6(2)	C(1)–Li(2)–Li(1a)	56.2(1)
C(6)–Li(2)–Li(1a)	106.7(2)	Li(1)–Li(2)–Li(2a)	59.1(1)
N(1)–Li(2)–Li(2a)	164.0(1)	C(1)–Li(2)–Li(2a)	103.5(1)
C(6)–Li(2)–Li(2a)	56.5(2)	Li(1a)–Li(2)–Li(2a)	59.2(1)
Li(1)–Li(2)–C(6a)	105.7(2)	N(1)–Li(2)–C(6a)	121.5(2)
C(1)–Li(2)–C(6a)	110.0(2)	C(6)–Li(2)–C(6a)	105.6(2)
Li(1a)–Li(2)–C(6a)	57.1(1)	Li(2a)–Li(2)–C(6a)	55.3(1)
Li(2)–N(1)–C(3)	99.4(2)	Li(2)–N(1)–C(4)	115.5(2)
C(3)–N(1)–C(4)	110.3(2)	Li(2)–N(1)–C(5)	112.4(2)
C(3)–N(1)–C(5)	110.6(2)	C(4)–N(1)–C(5)	108.5(2)
Li(1)–N(2)–C(8)	99.9(2)	Li(1)–N(2)–C(9)	111.1(2)
C(8)–N(2)–C(9)	110.7(2)	Li(1)–N(2)–C(10)	116.7(2)
C(8)–N(2)–C(10)	110.0(2)	C(9)–N(2)–C(10)	108.3(2)
Li(1)–C(1)–Li(2)	65.7(1)	Li(1)–C(1)–C(2)	148.5(2)
Li(2)–C(1)–C(2)	91.0(2)	Li(1)–C(1)–Li(1a)	68.4(2)
Li(2)–C(1)–Li(1a)	66.3(1)	C(2)–C(1)–Li(1a)	123.0(2)
C(1)–C(2)–C(3)	112.6(2)	N(1)–C(3)–C(2)	114.0(2)
Li(1)–C(6)–Li(2)	66.3(2)	Li(1)–C(6)–C(7)	91.1(2)
Li(2)–C(6)–C(7)	124.0(2)	Li(1)–C(6)–Li(2a)	65.7(1)
Li(2)–C(6)–Li(2a)	68.1(2)	C(7)–C(6)–Li(2a)	148.1(2)
C(6)–C(7)–C(8)	113.2(2)	N(2)–C(8)–C(7)	113.7(2)

TABLE 4

ANISOTROPIC TEMPERATURE FACTORS ($Å^2 \times 10^3$) [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li(1)	28(2)	24(2)	26(2)	1(2)	6(2)	3(2)
Li(2)	27(2)	23(2)	24(2)	0(2)	2(2)	−0(2)
N(1)	27(1)	20(1)	26(1)	−2(1)	5(1)	−1(1)
N(2)	26(1)	22(1)	27(1)	1(1)	5(1)	0(1)
C(1)	31(1)	27(1)	28(1)	−7(1)	12(1)	−8(1)
C(2)	31(2)	25(1)	36(1)	3(1)	6(1)	3(1)
C(3)	29(1)	28(1)	28(1)	3(1)	−2(1)	1(1)
C(4)	37(2)	32(1)	31(1)	−6(1)	−1(1)	2(1)
C(5)	31(2)	34(1)	40(2)	1(1)	4(1)	−6(1)
C(6)	28(1)	27(1)	29(1)	7(1)	−1(1)	−6(1)
C(7)	38(2)	25(1)	30(1)	−3(1)	9(1)	3(1)
C(8)	32(1)	30(1)	31(1)	1(1)	14(1)	6(1)
C(9)	37(2)	37(1)	29(1)	8(1)	9(1)	4(1)
C(10)	31(1)	33(1)	44(2)	3(1)	8(1)	−3(1)

[a] The anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + \ldots + 2hkabU_{12})$.

chelate ring conformation. Barriers to pseudorotation in heterocyclic five-membered rings which contain heavy atoms (and therefore a mix of long and short bonds) are high compared to barriers to pseudorotation in five-membered rings of first-row

TABLE 5

HYDROGEN COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($Å^2 \times 10^3$)

Atom	x	y	z	U
H(1a)	3604(24)	7240(32)	8515(10)	42
H(1b)	4127(26)	6725(27)	7839(11)	42
H(2a)	6104	8698	8118	45
H(2b)	5962	7208	8723	45
H(3a)	6537	10014	9277	45
H(3b)	4966	9639	9359	45
H(4a)	4669	14383	9051	44
H(4b)	5651	13253	9632	44
H(4c)	4074	12682	9457	44
H(5a)	6639	11785	8020	49
H(5b)	7192	12779	8746	49
H(5c)	6135	13849	8180	49
H(6a)	2008(24)	12873(27)	8296(12)	42
H(6b)	619(21)	12287(32)	7944(11)	41
H(7a)	508	12412	9110	47
H(7b)	1729	10939	9279	47
H(8a)	−863	9958	8522	42
H(8b)	−487	9585	9343	42
H(9a)	2040	7888	9550	48
H(9b)	1684	5811	9276	48
H(9c)	707	6853	9752	48
H(0a)	−1190	6910	8076	49
H(0b)	−1256	6316	8870	49
H(0c)	−263	5225	8417	49

TABLE 6

CRYSTALLOGRAPHIC DATA

Molecular formula:	$C_{10}H_{24}N_2Li_2$
Crystal system:	Monoclinic
Cell dimensions:	a 9.659(2), b 7.007(1), c 18.896(5) Å β 97.61(2)° V 1267 Å^3
Wavelength:	0.71069 Å (Mo-K_α, graphite monochromater)
Range of 2θ:	3.7–42°
Space group:	$P2/n$
Z:	4
Calculated density:	0.976 g/cm^3
Linear absorption coefficient Cm^{-1}:	0.52
Number of unique reflections:	1605
Structure factor weights:	$w = 1/[\sigma^2(F)+0.00020F^2]$ with $\sigma^2(F)$ from counting statistics
Final R factors:	$R = 0.0485$ $R_w = 0.0696$
Goodness of fit (Nominal):	3.302
Goodness of fit (Divided by slope of normal probability plot):	1.405
Crystal dimensions (mm):	0.25 × 0.25 × 0.35

elements [12], so it is likely that the ring conformations found in the crystal for **5** and **6** are close to the lowest energy conformation of the rings.

Figure 2 gives the torsion angles and bond lengths for the five-membered rings in

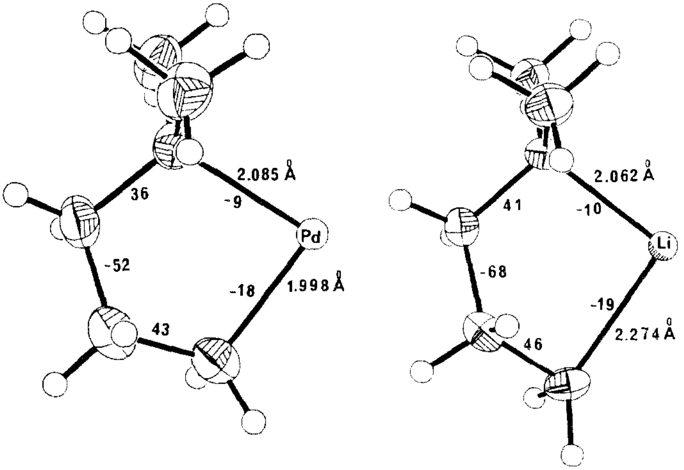

Fig. 2. Ring torsion angles and selected bond distances in the chelates Li(CH$_2$)$_3$NMe$_2$ and Pd(CH$_2$)$_3$NMe$_2$.

5 and 6. The values for 5 are for one of the two independent chelates, which, however, have virtually the same geometry. As can be seen, the two chelate rings in 5 and 6 have nearly identical conformations. The major differences between the two five-membered rings are, first, the longer C–Li bond (2.27 Å) compared to the C–Pd bond (2.00 Å) and second, the larger Pd–C(3)–C(2) angle (108.9°) compared to the Li–C(6)–C(7) angle of 91.1°. These differences produce a more puckered ring in 5, since the sum of the absolute values of the ring torsion angles in 5 is 183° vs. 158° for 6.

The similarity in conformation of the five-membered rings in 5 and 6 exists in spite of the different coordination geometries of the two metals. The palladium in 6 is square planar, while the lithium in 5 is part of a distorted cube and has a coordination number of seven (including the Li–Li interactions). Also different is the coordination of the carbon atom bonded to the metal. In the palladium chelate this carbon is a normal tetrahedral carbon, while for the lithium chelate the corresponding carbon has a coordination number of six. The close correlation in conformation between the chelate rings in 5 and 6 implies there are no bonding interactions present in the transition metal ring (such as an interaction with a β-hydrogen [13]) that are absent in the alkali metal ring. What differences exist can be accounted for by the longer C–Li vs. C–Pd bond, which would tend to produce a more puckered ring.

Acknowledgments

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References

1 W.N. Setzer and P. von R. Schleyer, X-ray Structural Analyses of Organolithium Compounds, Adv. in Organometal. Chem., P.G.W. thanks Prof. Schleyer for kindly providing a reprint of this review.
2 H.W. Gschwend and H.R. Rodriguez, Org. Reactions, 26 (1979) 1.
3 J.T.B.H. Jastrzebski, G. van Koten, K. Goubitz, C. Arlen and M. Pfeffer, J. Organomet. Chem., 246 (1983) C75.
4 G.W. Klumpp, P.J.A. Geurink, A.L. Spek and J.M. Duisenberg, J. Chem. Soc. Chem. Commun., (1983) 814.
5 J.T.B.H. Jastrzebski, G. van Koten, M. Konijn and C.H. Stam, J. Am. Chem. Soc., 104 (1982) 5490.
6 H. Dietrich and D. Rewicki, J. Organomet. Chem., 205 (1981) 281.
7 K.-H. Thiele, E. Langguth and G.E. Muller, Z. Anorg. Allg. Chem., 462 (1980) 152.
8 A. Shakoor, K. Jacob and K.-H. Thiele, Z. Anorg. Allg. Chem., 489 (1983) 115.
9 J.W. Suggs and K.S. Lee, J. Organomet. Chem., 299 (1986) 297.
10 E. Weiss and G. Hencken, J. Organomet. Chem., 21 (1970) 265; H. Dietrich, ibid., 205 (1981) 291.
11 H. Hope and P.P. Power, J. Am. Chem. Soc., 105 (1983) 5320.
12 F.G. Riddell, The Conformational Analysis of Heterocyclic Compounds, 1980, Academic Press, London, pp. 54–65; B. Fuchs in E.L. Eliel and N.L. Allinger (Eds.), Topics in Stereochemistry, Vol. 10, 1978, Wiley Interscience, New York.
13 M. Brookhart and M.L.H. Green, J. Organomet. Chem., 250 (1983) 395.