

Giving phenyllithium a right-handed double-helical twist. Syntheses and crystal structures of enantiopure alkyl-, aryl-, and amidolithium aggregates

Marcus Vestergren, Johan Eriksson, Göran Hilmersson, Mikael Håkansson*

Organic Chemistry, Department of Chemistry, Göteborg University, Kemivägen 10, SE-412 96 Göteborg, Sweden

Received 2 April 2003; received in revised form 12 June 2003; accepted 12 June 2003

Abstract

The influence of enantiopure nitrogen donor ligands on structure and aggregation in three lithium reagents has been investigated using single crystal X-ray diffraction methods. While the 1:1 complex between methyllithium and (–)-sparteine, $[\text{LiMe}(\text{spa})]_2$ (**1**), is dimeric, the 2:1 complex between phenyllithium and (–)-sparteine, $[\text{Li}_4\text{Ph}_4(\text{spa})_2]$ (**2**), displays a tetranuclear Li_4Ph_4 core with one sparteine ligand in each end. The core in **2** has a ladder-like structure, which resembles a double-helix in the sense that it is twisted corresponding to approximately one ninth of a full rotation. The stereochemistry is predetermined to a right-handed double-helix by the terminal sparteine ligands. Synthesis and structural characterization of homoleptic $[\text{Li}(\text{pypm})]_4$ (**3**), $\text{pypm} = (\text{S})$ -2-(1-pyrrolidinylmethyl)pyrrolidido, displays a tetramer with a helical twist analogous to **2**, which shows that this bidentate enantiopure amido ligand (pypm) also predetermines the chirality to a fragmented right-handed double-helix.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Organolithium; Enantiopure; Crystal structure; Double helix; Aggregation

1. Introduction

Lithium organyls frequently aggregate [1,2]. Polynuclear metal complexes with well-defined stereochemistry have potential applications as reagents, catalysts, functionalised materials, or molecular devices [3]. We use enantiopure ligands in conjunction with aggregating organometallic species with the aim of inducing self-assembly of new motifs and architectures that exhibit predetermined chirality. The alkaloid (–)-sparteine (Fig. 1), can be used as an enantiopure, bidentate N-donor ligand and is commercially available at a low cost. Organolithium complexes with (–)-sparteine are useful reagents for the enantioselective formation of new carbon–carbon bonds [4]. Despite this, structural data on sparteine-complexed organolithium reagents are very limited [5–11], although enantiopure *n*-butyllithium aggregates with other ligands have been reported [12].

Likewise, although the commercially available diamine (*S*)-2-(1-pyrrolidinylmethyl)pyrrolidine (Hpypm) (Fig. 1) can be treated with *n*-butyllithium to produce an enantiopure lithium amide reagent which is widely used for the enantioselective rearrangement of *meso*-epoxides to allylic alcohols [13–17], detailed structural information on such amidolithium aggregates—solvated or not—is still missing [18,19].

Organolithium reagents frequently form tetrameric aggregates in coordinating solvents (or whenever neutral ligands are present), as in e.g. $[(\text{Li}_4\text{Ph}_4(\text{Et}_2\text{O}))_4]$ [20], $[(\text{Li}_4\text{Ph}_4(\text{Me}_2\text{S}))_4]$ [21], or $[(\text{Li}_4\text{Me}_4(\text{tmeda}))_2]$ [22], while ladder-shaped aggregates are rare. The only lithium organyls that display ladder-like structures are Lewis base-free phenyllithium [23] and the 1:1 complex between *n*-butyllithium and (aminomethyl)(lithiomethyl)silane [24]. Homoleptic lithium amides, on the other hand, seem to prefer ladder-like structures. Stacking of $\text{Li}_2(\text{NR}_2)_2$ units (giving e.g. cubane structures) has been predicted to be energetically unfavourable [25] (Fig. 2); this idea has found support in calculations [26]. Conclusive structural data are often missing due to the polymeric nature of

* Corresponding author. Tel.: +46-31-772-2896; fax: +46-31-772-3840.

E-mail address: hson@organic.gu.se (M. Håkansson).

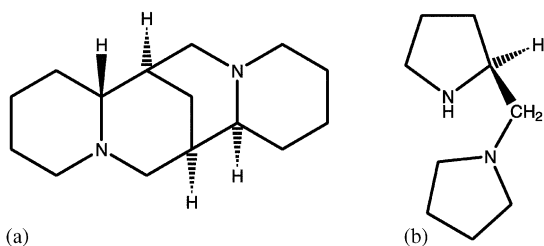


Fig. 1. Showing (a) (–)-sparteine (spa) and (b) (S)-2-(1-pyrrolidinylmethyl)pyrrolidine (Hpypmp).

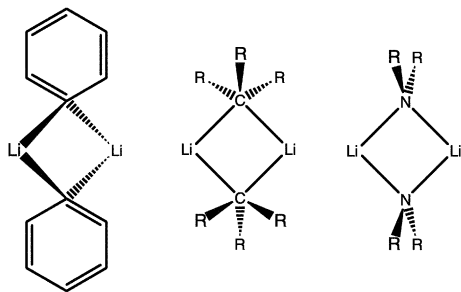


Fig. 2. Stacking of dimers is often encountered in lithium alkyls and aryls, while lithium amides prefer laddered structures for steric reasons.

such amides, but tetranuclear [25,27], pentanuclear [28], and octanuclear [29] ladder fragments with achiral or racemic ligands have been structurally characterized and provide indirect evidence of laddering in polymeric amides. Indeed, two crystal structures of laddered polymeric lithium amides have been reported, i.e. $[\text{Li}(\text{NHCH}_2\text{CH}_2\text{NH}_2)]$ [30] and $[\text{PhCH}_2\text{N}(\text{H})\text{Li}]_2 \cdot \text{H}_2\text{NCH}_2\text{Ph}$ [31]. On the other hand, lithium diisopropylamide crystallizes as a single-chain helix, with right- and left-handed helices in equal amounts in the crystal [32].

2. Experimental

2.1. General

All operations were carried out under nitrogen using Schlenk, glove box, or low temperature [33] techniques. Solvents were distilled from sodium/benzophenone shortly prior to use. (–)-Sparteine and (S)-2-(1-pyrrolidinylmethyl)pyrrolidine were distilled from CaH_2 , deoxygenated, and finally treated with 4 Å molecular sieves. Commercial (Aldrich) organolithium reagents were used as delivered.

2.2. Preparation of $[\text{Li}_2\text{Me}_2(\text{spa})_2]$ (1)

Dry (–)-sparteine (0.2 ml, 0.9 mmol) was added dropwise from a syringe (along the side of the Schlenk tube) to a 1.6 M solution of methylolithium in Et_2O (5.0

ml, 8.0 mmol) at ambient temperature. The resulting colourless solution was kept completely still (at ambient temperature) and started to deposit colourless crystals of **1** after a few minutes. Probably on account of the short crystallization time, these crystals were small and of poor X-ray quality, but repeated attempts to grow better crystals failed. Yield: 0.14 g, 61%.

2.3. Preparation of $[\text{Li}_4\text{Ph}_4(\text{spa})_2]$ (2)

Dry (–)-sparteine (0.2 ml, 0.9 mmol) was added dropwise from a syringe to a 1.8 M solution of phenyllithium (5 ml, 9.0 mmol) in cyclohexane/ Et_2O (70/30) at ambient temperature. The resulting dark solution was kept at ambient temperature and colourless crystals of **2** started to grow after a few hours. Yield: 0.10 g, 25%.

2.4. Preparation of $[\text{Li}_4(\text{pypmp})_4]$ (3)

(S)-1-(2-Pyrrolidinylmethyl)pyrrolidine (0.028 g, 0.18 mmol) was dissolved in 1 ml of toluene- d_8 . Freshly prepared halide- and solvent-free $[\text{Li}^6\text{Li}]n$ -butyllithium [34] (20 μl , 0.20 mmol) was added to the solution at 0 °C. After 1 h at –80 °C, colourless crystals of the lithium salt of (S)-1-(2-pyrrolidinylmethyl)pyrrolidine formed. Approximate yield: 30%.

2.5. X-ray crystallography

Crystal and experimental data are summarised in Table 1. All crystals were selected and mounted under nitrogen in a glass capillary at low temperature [33] and transferred in liquid nitrogen to either a Rigaku AFC6 diffractometer (**1** and **3**) or a Rigaku R-AXIS IIC image plate system (**2**). Diffracted intensities were measured using graphite-monochromated $\text{Mo-K}\alpha$ ($\lambda = 0.71073$ Å) radiation from a RU200 rotating anode operated at 50 kV and 90 (R-AXIS) or 180 mA (AFC6). With the AFC6 diffractometer, stationary background counts were recorded on each side of a reflection, the ratio of peak counting time to background counting time being 2:1. Weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections were monitored regularly after measurement of 150 reflections and indicated crystal stability during the diffraction experiment. Cell constants were obtained by least-squares refinement from the setting angles of 20 reflections. No correction was made for the effects of absorption owing to lack of suitable reflections for which azimuthal scans could be collected. With the R-AXIS IIC detector, 90 oscillation photos with a rotation angle of 2° were collected and processed using the CrystalClear software package. An empirical absorption correction was applied using the REQAB program under

Table 1
Crystal and refinement data for [Li₂Me₂(spa)₂] (**1**), [Li₄Ph₄(spa)₂] (**2**), and [Li₄(pypm)₄] (**3**)

Compound	1	2	3
Empirical formula	C ₁₆ H ₂₉ LiN ₂	C ₂₇ H ₃₆ Li ₂ N ₂	C ₃₆ H ₆₈ Li ₄ N ₈
Formula weight	256.35	402.46	640.74
Temperature (K)	153	123	153
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2	<i>C</i> 2	<i>P</i> 2 ₁
Unit cell dimensions			
<i>a</i> (Å)	13.423(4)	13.894(5)	9.247(6)
<i>b</i> (Å)	10.427(2)	17.630(6)	15.832(3)
<i>c</i> (Å)	11.102(3)	9.599(4)	13.650(5)
α (°)	90	90	90
β (°)	90	102.668(10)	103.93(4)
γ (°)	90	90	90
<i>V</i> (Å ³)	1553.8(7)	2294.1(14)	1939.7(14)
<i>Z</i>	4	4	2
<i>D</i> _{calc} (Mg m ⁻³)	1.096	1.165	1.097
Absorption coefficient (mm ⁻¹)	0.063	0.066	0.064
Crystal size (mm ³)	0.10 × 0.10 × 0.10	0.15 × 0.15 × 0.15	0.15 × 0.15 × 0.15
Reflections collected	1152	7143	3770
Independent reflections	1152	3957 [<i>R</i> _{int} = 0.0726]	3541 [<i>R</i> _{int} = 0.0462]
Completeness to $\theta = 25.00^\circ$	96.3% ($\theta = 22.5^\circ$)	98.8%	99.8%
Data/restraints/parameters	1152/0/171	3957/1/424	3541/1/443
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0421, <i>wR</i> ₂ = 0.0488	<i>R</i> ₁ = 0.0632, <i>wR</i> ₂ = 0.1250	<i>R</i> ₁ = 0.0456, <i>wR</i> ₂ = 0.1114
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.2797, <i>wR</i> ₂ = 0.0881	<i>R</i> ₁ = 0.0889, <i>wR</i> ₂ = 0.1352	<i>R</i> ₁ = 0.1390, <i>wR</i> ₂ = 0.1444
Largest difference peak and hole (e Å ⁻³)	0.208 and -0.232	0.181 and -0.187	0.236 and -0.214

CrystalClear. Crystal and refinement data for compounds **1**–**3** are summarized in Table 1. All structures were solved by direct methods (SIR 97) [35] and refined using full-matrix least-squares calculations on *F*² (SHELXL-97) [36] operating in the WinGX program package [37]. Anisotropic thermal displacement parameters were refined for all the non-hydrogen atoms, except for the methyl carbon (C16) in compound **1**, which was refined isotropically. The hydrogen atoms on this carbon were located from a difference map, and allowed to refine without constraints. They displayed large shifts during refinement and are probably disordered, but on account of the low quality data (only small crystals of poor quality and diffracting power could be obtained) no attempt to model the disorder was made. All other hydrogen atoms were included in calculated positions and refined using a riding model or, as in compound **2**, allowed to refine without any positional constraints. In compound **3**, carbon C(8) was disordered on two sites. The occupancy refined to 0.64/0.36 for the C(8A)/C(8B) pair. Structural illustrations have been drawn with ORTEP-3 for Windows [38] and PLUTON [39] under WinGX.

3. Results and discussion

It is likely that simple lithium alkyls and aryls prefer hexameric aggregates in non-coordinating solvents, as indicated by the crystal structures of [Li₆(*n*-Bu)₆] [40]

and [(Li₆(C₆H₃-3,5-*t*Bu₂)₆)] [41]. An even higher degree of aggregation may be possible to attain since Lewis base-free LiPh has been shown to be polymeric in the solid state (by a crystal structure determination from powder data) [23], and organolithium compounds with aggregation numbers of eight and nine have been detected in solution at low temperatures [42]. Such larger aggregates are broken down when coordinating solvents or ligands are introduced, resulting in e.g. cubanes, dimers, or monomers. In order to maximise the chance of obtaining large aggregates displaying new chiral superstructures, we chose to use a tenfold excess of organolithium reagents over the neutral (–)-sparteine ligand in the solutions from which the crystals were isolated. We reasoned that a low ratio of ligand to lithium should be sufficient to induce chiral self-assembly and predetermine the stereochemistry.

In the LiMe case, regardless of the solution composition, only a phase with a relatively high sparteine content could be obtained. The 1:1 complex [Li₂Me₂(spa)₂] (**1**) between methyllithium and (–)-sparteine is dimeric (Figs. 3 and 4), and although it is similar to the well-known dimeric aryllithium complexes with bidentate neutral ligands, represented by e.g. [Li₂Ph₂(tmeda)₂] [43] or [(Li₂Mes₂(THF)₄] (Mes = mesityl) [44], it is nevertheless the first crystal structure featuring a Li₂Me₂ dimer. Such dimeric Li₂Me₂ units may be regarded as building blocks for cubane—as well as ladder-shaped structures, but not for the lithium tetrahedra found in [Li₄Me₄] [45,46] that are face-

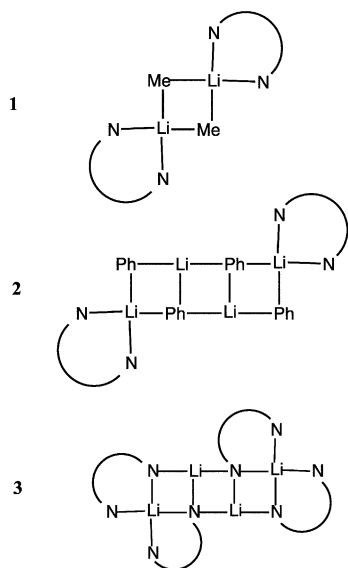


Fig. 3. Schematic representation of $[\text{Li}_2\text{Me}_2(\text{spa})_2]$ (1), $[\text{Li}_4\text{Ph}_4(\text{spa})_2]$ (2), and $[\text{Li}_4(\text{pymp})_4]$ (3).

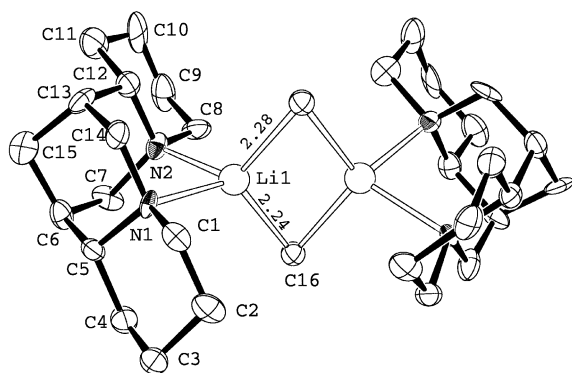


Fig. 4. Methyl lithium and (–)-sparteine form dimeric $[\text{Li}_2\text{Me}_2(\text{spa})_2]$ (1). ORTEP drawing showing the crystallographic numbering in (1). Hydrogen atoms are omitted for clarity. Thermal ellipsoids enclose 50% probability.

capped by the methyl groups. The $\text{Li}\cdots\text{Li}$ distance in **1** is 2.49(4) Å (Table 2), and thus not indicative of any substantial metal–metal bonding interaction. The brid-

Table 2
Selected interatomic distances (Å) and angles ($^\circ$) for $[\text{Li}_2\text{Me}_2(\text{spa})_2]$ (1)

Bond lengths			
Li(1)–N(1)	2.13(2)	Li(1)–N(2)	2.15(2)
Li(1)–C(16)	2.24(3)	Li(1)–C(16) ^a	2.28(2)
Li(1)–Li(1) ^a	2.49(4)	N(1)–C(14)	1.464(11)
N(1)–C(1)	1.495(11)	N(1)–C(5)	1.501(12)
Bond angles			
N(1)–Li(1)–N(2)	83.6(8)	N(1)–Li(1)–C(16)	125.1(10)
N(2)–Li(1)–C(16)	107.0(11)	N(1)–Li(1)–C(16) ^a	104.7(10)
N(2)–Li(1)–C(16) ^a	121.3(10)	C(16)–Li(1)–C(16) ^a	113.1(10)
C(16) ^a –Li(1)–Li(1) ^a	55.8(9)	Li(1)–C(16)–Li(1) ^a	66.8(10)

^a Symmetry code: $-x, -y+2, z$.

ging methyl groups form nearly symmetrical 3c,2e-bonds with the two lithium ions as seen from the two Li–C bond distances of 2.24(3) and 2.28(2) Å, which are somewhat shorter (but not significantly) than the average Li–C bond length found for sp^3 -hybridized carbon atoms bonded to bridging lithium atoms of 2.29 Å [1]. The Li_2C_2 ring in **1** is nearly planar, i.e. the deviation from the least-squares plane through the four central atoms is 0.026 Å. The C1–Li1–C2 angle of 113° and the N1–Li1–N2 of 84° give evidence of a distorted tetrahedral geometry around lithium, and a bite angle slightly less than 90° is typical for the sparteine ligand. In **1**, the neutral ligands are coordinated by Li at distances of 2.13 and 2.15 Å, which compares well to the organolithium–sparteine complexes described in the Cambridge Structural Database [5–11]. The methyl and sparteine ligands efficiently cover the lithium ions with a hydrocarbon surface, thus making the complex readily soluble in many organic solvents but possibly less suitable as a reagent. It is probable that for larger R-groups (as compared to methyl) steric hindrance will disfavour the dimer.

In contrast to **1**, we find that phenyllithium and (–)-sparteine form the 2:1 complex $[\text{Li}_4\text{Ph}_4(\text{spa})_2]$ (**2**), which displays a tetranuclear Li_4Ph_4 core with one sparteine ligand in each end (Figs. 3 and 5). The core has a ladder-like structure, which resembles a double-helix (see Fig. 6) in the sense that it is twisted corresponding to approximately one ninth of a full rotation. This approximation is based on the fact that the middle rung is twisted approximately 39° , i.e. the Li(2)–C(16)–Li(2)*–C(16)* torsion angle is $38.8(3)^\circ$. Disregarding the terminal rungs, which incorporate sparteine and thus are atypical, there would then have to be nine middle rungs connected to complete a full turn of the helix. The chirality of **2** is predetermined [3] to a right-handed double-helix by the terminal sparteine ligands. Crystallographically, the molecule consists of two equivalent parts that are related by a two-fold rotation axis. One can describe the molecule as being put together by two $[\text{Li}_2\text{Ph}_2(\text{spa})_2]$ dimers, which each has lost one sparteine ligand, but the short Li(2)–C(16)* and Li(2)*–C(16) bonds of 2.235(7) Å underline that the two halves are firmly fixed together. There are two crystallographically different lithium atoms—four-coordinate Li(1) and three-coordinate Li(2)—in **2**. The coordination geometry around the terminal Li(1) is best described as a distorted tetrahedron: Li(1) coordinates the two nitrogen atoms of a sparteine ligand and two bridging phenyl groups; see Table 3 for bond distances and angles. This bonding pattern is typical for the dimeric $[\text{Li}_2\text{R}_2(\text{LL})_2]$ units found in e.g. $[\text{Li}_2\text{Ph}_2(\text{tmeda})_2]$ [43] or $[\text{Li}_2\text{Me}_2(\text{spa})_2]$ (**1**). The coordination geometry around Li(2) (Fig. 7), is distorted trigonal planar with Li(2) situated in the plane spanned by C(16), C(22) and C(16)*. While the bridging mode for the C(22)–C(27)

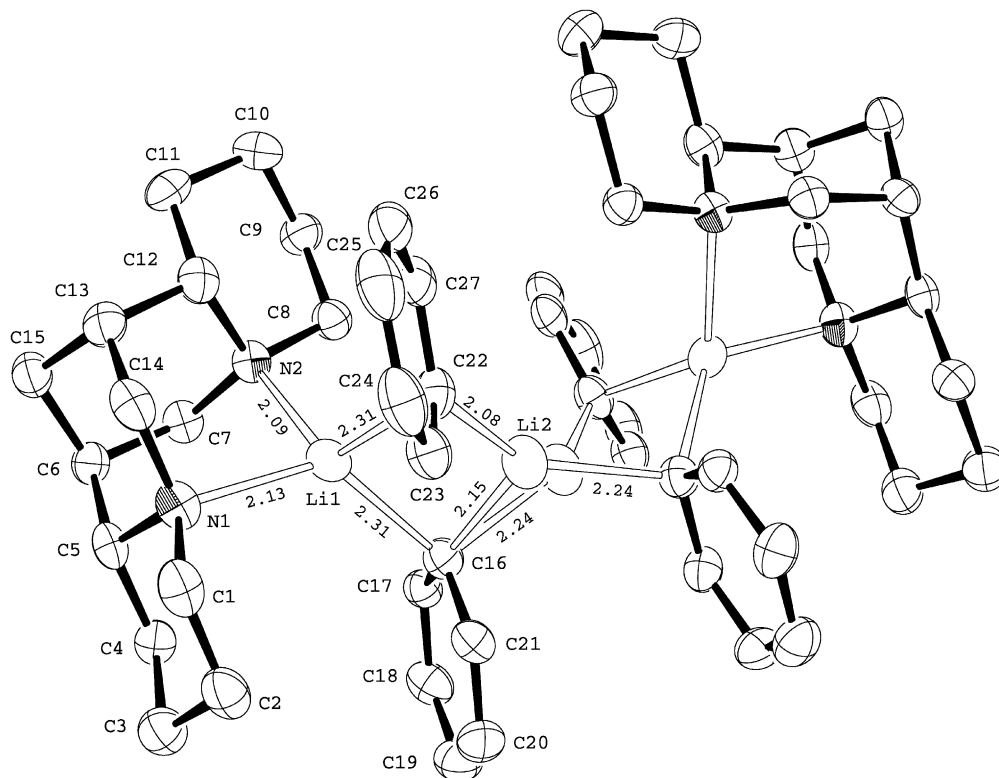


Fig. 5. Tetranuclear $[\text{Li}_4\text{Ph}_4(\text{spa})_2]$ (**2**) displays a chiral ladder-structure. ORTEP drawing showing the crystallographic numbering in (**2**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids enclose 50% probability.

phenyl ring is unremarkable (but note the short $\text{Li}(2)\text{--C}(22)$ bond of $2.075(7)$ Å, the *ipso* carbon in the $\text{C}(16)\text{--}$

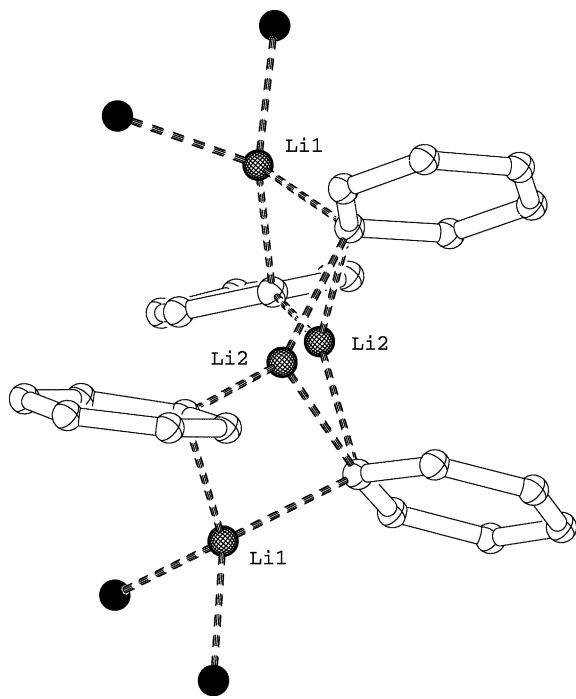


Fig. 6. The twist in $[\text{Li}_4\text{Ph}_4(\text{spa})_2]$ (**2**) resembles one ninth of a full turn in a double helix. Only right-handed double-helix fragments are found in crystals of **2**. The carbon atoms of the sparteine ligands have been omitted for clarity.

$\text{C}(21)$ phenyl group bridges three lithium atoms in an unusual pattern (Fig. 7), with $\text{Li}\text{--C}$ interactions from 2.15 to 2.31 Å. Moreover, the *ortho* carbon atoms display short $\text{Li}\text{--C}$ distances in the 2.48–2.50 Å range, while the *meta* and *para* carbon atoms do not interact with lithium, in contrast to the π -bonding arrangement found in base-free phenyllithium [23]. Along with the $\text{Li}\text{--C}(\text{ortho})$ interactions go relatively short $\text{Li}\text{--H}$ contacts as exemplified by the $\text{Li}(2)\text{--H}(21)$ distance of $2.25(5)$ Å. Both crystallographically unique phenyl groups show the usual structural consequences of lithiation: the $\text{C}(\text{ipso})\text{--C}(\text{ortho})$ distances are lengthened and the $\text{C}\text{--C}\text{--C}$ angle around the *ipso* carbon is smaller than the other $\text{C}\text{--C}\text{--C}$ angles in the phenyl ring. The bonding situation is similar to that found in the $[\text{Li}_6(\text{C}_6\text{H}_3\text{--}3,5\text{--}^t\text{Bu}_2)_6]$ hexamer, where each aryl group cap one of eight triangular Li_3 faces, but in **2** one of the $\text{Li}\text{--Li}$ edges is much longer, i.e. $3.803(13)$ Å. This difference is also reflected in the $\text{Li}(1)\text{--Li}(2)\text{--Li}(2)^*$ angle of $99.0(3)^\circ$. As an alternative to being formed from two dimers, one might consider **2** as having been formed from hexameric Li_6Ph_6 aggregates (similar to the $[\text{Li}_6(\text{C}_6\text{H}_3\text{--}3,5\text{--}^t\text{Bu}_2)_6]$ hexamer), which have been broken up by sparteine ligands. In order to determine if the tetranuclear helical core **2** is retained in solution, NMR studies of phenyllithium/sparteine aggregates in THF/DEE/toluene is underway.

Table 3
Selected interatomic distances (Å) and angles (°) for [Li₄Ph₄(spa)₂] (2)

Bond lengths			
Li(1)–N(2)	2.090(6)	Li(1)–N(1)	2.133(6)
Li(1)–C(16)	2.310(7)	Li(1)–C(22)	2.314(7)
Li(1)–Li(2)	2.527(8)	Li(2)–C(22)	2.075(7)
Li(2)–C(16)	2.153(7)	Li(2)–C(16) ^a	2.235(7)
Li(2)–Li(2) ^a	2.472(12)	Li(2)–C(21)	2.478(7)
Li(2)–C(17) ^a	2.496(7)	C(16)–C(17)	1.398(5)
C(16)–C(21)	1.417(5)	C(16)–Li(2) ^a	2.235(7)
C(17)–C(18)	1.386(5)	C(17)–Li(2) ^a	2.496(7)
C(18)–C(19)	1.381(6)	C(19)–C(20)	1.373(6)
C(20)–C(21)	1.384(5)	C(22)–C(27)	1.412(5)
C(22)–C(23)	1.417(5)	C(23)–C(24)	1.384(6)
C(24)–C(25)	1.377(7)	C(25)–C(26)	1.360(6)
Bond angles			
N(2)–Li(1)–N(1)	87.3(2)	N(2)–Li(1)–C(16)	111.9(3)
N(1)–Li(1)–C(16)	128.2(3)	N(2)–Li(1)–C(22)	120.4(3)
N(1)–Li(1)–C(22)	109.0(3)	C(16)–Li(1)–C(22)	101.6(3)
C(22)–Li(2)–C(16)	115.9(3)	C(22)–Li(2)–C(16) ^a	145.8(3)
C(16)–Li(2)–C(16) ^a	98.3(3)	C(22)–Li(2)–C(21)	112.7(3)
C(16) ^a –Li(2)–C(21)	94.6(3)	Li(2) ^a –Li(2)–C(21)	79.5(2)
C(22)–Li(2)–C(17) ^a	115.2(3)	C(16)–Li(2)–C(17) ^a	124.8(3)
C(16)–Li(2)–Li(1)	58.5(2)	C(16) ^a –Li(2)–Li(1)	152.9(3)
C(17)–C(16)–C(21)	112.3(3)	C(17)–C(16)–Li(2)	151.7(3)
C(17)–C(16)–Li(2) ^a	83.4(3)	C(21)–C(16)–Li(2) ^a	118.5(3)
Li(2)–C(16)–Li(2) ^a	68.6(3)	C(17)–C(16)–Li(1)	122.6(3)
C(21)–C(16)–Li(1)	106.0(3)	Li(2)–C(16)–Li(1)	68.9(2)
Li(2) ^a –C(16)–Li(1)	113.6(3)	C(18)–C(17)–C(16)	124.8(3)
C(18)–C(17)–Li(2) ^a	126.9(3)	C(16)–C(17)–Li(2) ^a	62.8(2)
C(19)–C(18)–C(17)	119.6(4)	C(20)–C(19)–C(18)	119.1(4)
C(19)–C(20)–C(21)	119.9(3)	C(20)–C(21)–C(16)	124.3(3)
C(20)–C(21)–Li(2)	160.0(3)	C(16)–C(21)–Li(2)	60.0(2)
C(23)–C(22)–C(23)	113.2(3)	C(23)–C(22)–Li(2)	115.8(3)
C(27)–C(22)–Li(1)	113.9(3)	Li(2)–C(22)–Li(1)	70.1(2)
C(24)–C(23)–C(22)	122.6(4)	C(25)–C(24)–C(23)	120.5(4)
C(26)–C(25)–C(24)	119.1(4)	C(25)–C(26)–C(27)	120.5(4)
C(26)–C(27)–C(22)	124.0(4)	C(21)–Li(2)–C(17) ^a	104.8(3)

^a Symmetry code: $-x+2, y, -z+1$.

We also report synthesis and structural characterization of the homoleptic tetramer [Li₄(pypm)₄] (3), pypm = (S)-2-(1-pyrrolidinylmethyl)pyrrolidido, which displays a helical twist similar to that exhibited by phenyllithium in **2** (Figs. 8 and 9 and Table 4). The enantiopure amido ligand in **3** predetermines the chirality—just as (–)-sparteine does in **2**—to a right-handed double-helix. This implies that it might be possible to prepare double-helical lithium amide polymers with predetermined handedness using the appropriate amido ligands. In **3**, the N(2)–Li(1)–N(4)–Li(2) torsion angle is 13.0(3)°, the Li(2)–N(4)–Li(3)–N(5) torsion angle is 20.9(4)°, and the Li(2)–N(4)–Li(3)–N(5) torsion angle is 13.5(3)°, which results in a smooth double-helical twist and means that the three rungs are twisted (in total) approximately 47°. Apart from this twisting, Li–N bond distances (average 2.05 Å) and angles in the ladder rungs are similar to those found in related lithium amides [47], e.g. the tetranuclear, laddered TMEDA complex of pyrrolididolithium [25]. The

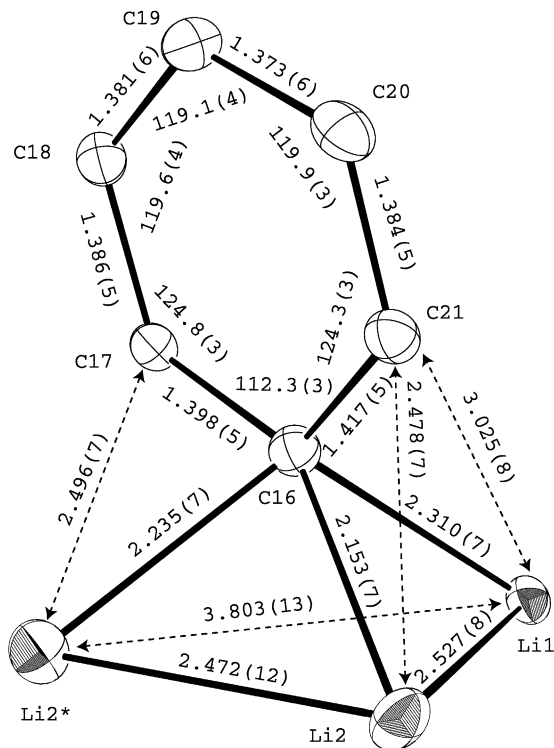


Fig. 7. ORTEP drawing of the coordination geometry around C(16) in [Li₄Ph₄(spa)₂] (2). Interatomic distances are given in Ångstrom and bond angles in degrees.

four-coordinate, terminal Li(1) and Li(4) exhibit distorted tetrahedral (N–Li–N angles coordination figures), while three-coordinate Li(2) and Li(3) have approximately trigonal planar coordination geometry.

Table 4
Selected interatomic distances (Å) and angles (°) for [Li₄(pypm)₄] (3)

Bond lengths			
Li(1)–N(2)	1.974(10)	Li(1)–N(3)	2.077(10)
Li(1)–N(1)	2.164(9)	Li(1)–N(4)	2.188(9)
Li(1)–Li(2)	2.388(12)	Li(1)–C(5)	2.749(10)
Li(1)–C(14)	2.765(10)	Li(2)–N(2)	1.972(9)
Li(2)–N(4)	2.037(10)	Li(2)–N(5)	2.064(9)
Li(2)–Li(3)	2.375(11)	Li(2)–C(24)	2.742(10)
Li(3)–N(7)	1.952(9)	Li(3)–N(5)	2.051(10)
Li(3)–N(4)	2.078(9)	Li(3)–Li(4)	2.361(11)
Li(3)–C(18)	2.728(10)	Li(3)–C(36)	2.773(11)
Li(4)–N(7)	1.987(9)	Li(4)–N(6)	2.069(9)
Li(4)–N(8)	2.133(9)	Li(4)–N(5)	2.150(9)
Li(4)–C(32)	2.705(10)	Li(4)–C(23)	2.757(10)
Bond angles			
N(2)–Li(1)–N(3)	131.6(4)	N(2)–Li(1)–N(1)	87.3(4)
N(3)–Li(1)–N(1)	121.2(4)	N(2)–Li(1)–N(4)	103.9(4)
N(3)–Li(1)–N(4)	88.4(4)	N(1)–Li(1)–N(4)	128.4(4)
N(2)–Li(2)–N(4)	109.8(4)	N(2)–Li(2)–N(5)	143.7(5)
N(4)–Li(2)–N(5)	106.3(4)	N(7)–Li(3)–N(5)	110.2(4)
N(7)–Li(3)–N(4)	144.1(5)	N(5)–Li(3)–N(4)	105.3(4)
N(7)–Li(4)–N(6)	128.0(4)	N(7)–Li(4)–N(8)	88.4(4)
N(6)–Li(4)–N(8)	120.4(4)	N(7)–Li(4)–N(5)	105.0(4)
N(6)–Li(4)–N(5)	90.2(4)	N(8)–Li(4)–N(5)	128.3(4)

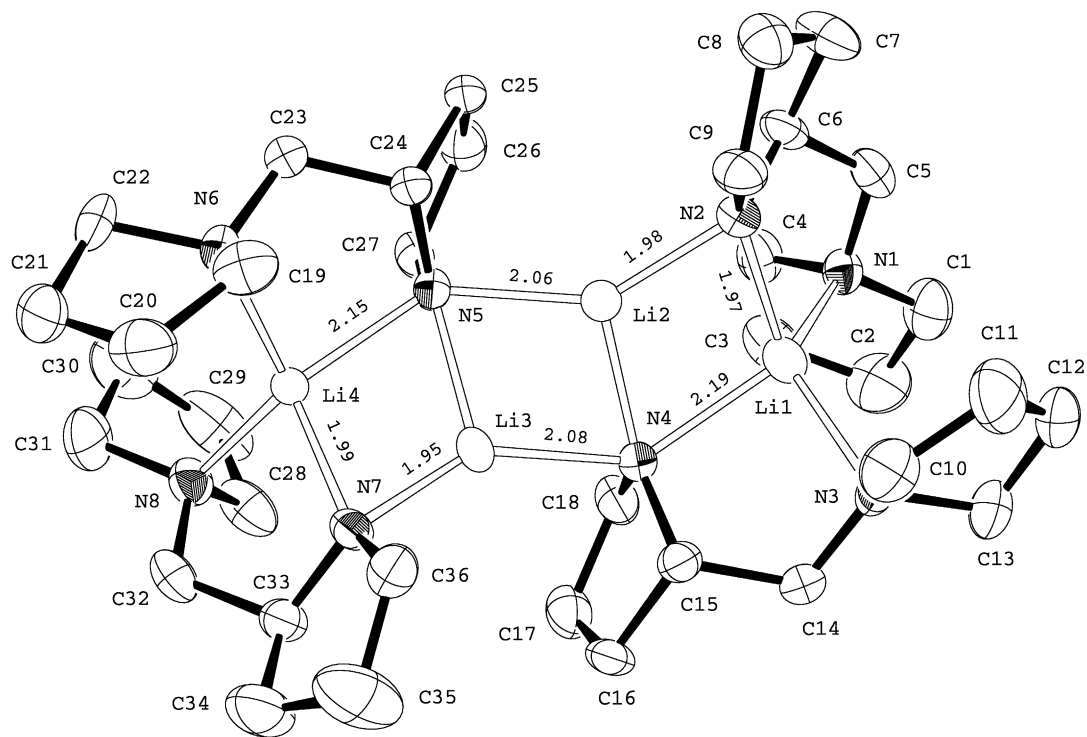


Fig. 8. ORTEP drawing showing the crystallographic numbering in tetrameric, laddered $[\text{Li}_4(\text{pymp})_4]$ (**3**). Hydrogen atoms are omitted for clarity. Thermal ellipsoids enclose 50% probability.

It is obvious that an increased aggregation, i.e. a lengthening of the ladder would also increase the proportion of four-coordinate lithium atoms, which

may become a decisive factor in non-coordinating solvents. On the other hand, a cyclic trimer of a related lithium amide (which should display exclusively three-coordinate lithium atoms) has been identified in toluene solution from NMR data [48].

The double-helical Li_4R_4 ladder fragment in **2** is a new motif in organolithium chemistry which emphasizes that laddering and thus potential double-helicity is not restricted to lithium amides. On the contrary, taking into account the laddered structure of base-free phenyllithium [23], one can now suggest that also homoleptic organolithium compounds may form double-helices in the solid state, perhaps even without induction from chiral ligands. It might thus be possible to prepare a double-helical aryllithium oligo- or polymer, using appropriate achiral substituents, and since this double-helix most likely would be labile, crystallization as a conglomerate would open up the possibility of enantioselective synthesis of e.g. the right-handed helix by total spontaneous resolution.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 205642 for compound **1**, 205643 for compound **2**, and 205644 for compound **3**. Copies of this information may

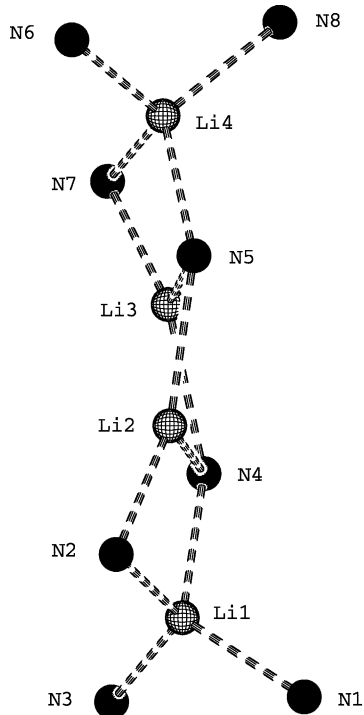


Fig. 9. Crystals of **3** contain enantiopure (right-handed) double-helix fragments. Carbon and hydrogen atoms are omitted for clarity.

be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

Financial support from the Swedish Research Council/Swedish Natural Science Research Council (VR/NFR) is gratefully acknowledged. Preparative assistance from Mari Carlsson and Sofie Jönsson is much appreciated.

References

- [1] W.N. Setzer, P. v.R. Schleyer, *Adv. Organomet. Chem.* 24 (1985) 353.
- [2] E. Weiss, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1501.
- [3] U. Knof, A. Von Zelewsky, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 303.
- [4] D. Hoppe, T. Hense, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2282.
- [5] I. Hoppe, M. Marsch, K. Harms, G. Boche, D. Hoppe, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2158.
- [6] M. Marsch, K. Harms, O. Zschage, D. Hoppe, G. Boche, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 321.
- [7] D.J. Pippel, G.A. Weisenburger, S.R. Wilson, P. Beak, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 2522.
- [8] G. Boche, M. Marsch, J. Harbach, K. Harms, B. Ledig, F. Schubert, J.C.W. Lohrenz, H. Ahlbrecht, *Chem. Ber.* 126 (1993) 1887.
- [9] R.I. Papasergio, B.W. Skelton, P. Twiss, A.H. White, C.L. Raston, *J. Chem. Soc. Dalton Trans.* (1990) 1161.
- [10] L.T. Byrne, L.M. Engelhardt, G.E. Jacobsen, W.P. Leung, R.I. Papasergio, C.L. Raston, B.W. Skelton, P. Twiss, A.H. White, *J. Chem. Soc. Dalton Trans.* (1989) 105.
- [11] F. Marr, R. Frohlich, D. Hoppe, *Tetrahedron: Asymmetry* 13 (2002) 2587.
- [12] B. Goldfuss, M. Steigelmann, F. Rominger, H. Urtel, *Chem.—Eur. J.* 7 (2001) 4456.
- [13] P.I. Arvidsson, A.Z.-Q. Khan, G. Hilmersson, O. Davidsson, M. Hakansson, *Enantiomer* 4 (1999) 445.
- [14] M. Asami, *Chem. Lett.* (1984) 829.
- [15] M. Asami, *Bull. Chem. Soc. Jpn.* 63 (1990) 1402.
- [16] M. Asami, *Bull. Chem. Soc. Jpn.* 63 (1990) 721.
- [17] P. O'Brien, P. Poumellec, *J. Chem. Soc. Perkin Trans.* (1998) 2435.
- [18] P.I. Arvidsson, G. Hilmersson, P. Ahlberg, *J. Am. Chem. Soc.* 121 (1999) 1883.
- [19] P.I. Arvidsson, P. Ahlberg, G. Hilmersson, *Chemistry* 5 (1999) 1348.
- [20] H. Hope, P.P. Power, *J. Am. Chem. Soc.* 105 (1983) 5320.
- [21] M.M. Olmstead, P.P. Power, *J. Am. Chem. Soc.* 112 (1990) 8008.
- [22] H. Koester, D. Thoennes, E. Weiss, *J. Organomet. Chem.* 160 (1978) 1.
- [23] R.E. Dinnebier, U. Behrens, F. Olbrich, *J. Am. Chem. Soc.* 120 (1998) 1430.
- [24] C. Strohmann, B.C. Abele, *Organometallics* 19 (2000) 4173.
- [25] D.R. Armstrong, D. Barr, W. Clegg, S.M. Hodgson, R.E. Mulvey, D. Reed, R. Snaith, D.S. Wright, *J. Am. Chem. Soc.* 111 (1989) 4719.
- [26] M.G. Gardiner, C.L. Raston, *Inorg. Chem.* 35 (1996) 4047.
- [27] B.L. Lucht, D.B. Collum, *J. Am. Chem. Soc.* 118 (1996) 3529.
- [28] W. Clegg, S.T. Liddle, R.E. Mulvey, A. Robertson, *Chem. Commun.* (2000) 223.
- [29] N.D.R. Barnett, W. Clegg, L. Horsburgh, D.M. Lindsay, Q.-Y. Liu, F.M. Mackenzie, R.E. Mulvey, P.G. Williard, *Chem. Commun.* (1996) 2321.
- [30] G.R. Kowach, C.J. Warren, R.C. Haushalter, F.J. DiSalvo, *Inorg. Chem.* 37 (1998) 156.
- [31] A.R. Kennedy, R.E. Mulvey, A. Robertson, *Chem. Commun.* (1998) 89.
- [32] N.D.R. Barnett, R.E. Mulvey, W. Clegg, P.A. Oneil, *J. Am. Chem. Soc.* 113 (1991) 8187.
- [33] M. Hakansson, *Inorg. Synth.* 32 (1998) 222.
- [34] G. Hilmersson, O. Davidsson, *J. Organomet. Chem.* 489 (1995) 175.
- [35] A. Altomare, M.C. Burla, M. Camalli, G.L. Casciarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 32 (1999) 115.
- [36] G.M. Sheldrick, *SHELX97—Programs for Crystal Structure Analysis (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- [37] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [38] L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.
- [39] A.L. Spek, *PLATON. A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 2002.
- [40] T. Kottke, D. Stalke, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 580.
- [41] R.J. Wehmschulte, P.P. Power, *J. Am. Chem. Soc.* 119 (1997) 2847.
- [42] G. Fraenkel, M. Henrichs, J.M. Hewitt, B.M. Su, M.J. Geckle, *J. Am. Chem. Soc.* 102 (1980) 3345.
- [43] D. Thoennes, E. Weiss, *Chem. Ber.* 111 (1978) 3157.
- [44] M.A. Beno, H. Hope, M.M. Olmstead, P.P. Power, *Organometallics* 4 (1985) 2117.
- [45] E. Weiss, G. Hencken, *J. Organomet. Chem.* 21 (1970) 265.
- [46] E. Weiss, T. Lambertsen, B. Schubert, J.K. Cockcroft, A. Wiedenmann, *Chem. Ber.* 123 (1990) 79.
- [47] R.E. Mulvey, *Chem. Soc. Rev.* 20 (1991) 167.
- [48] P.I. Arvidsson, O. Davidsson, *Angew. Chem. Int. Ed. Engl.* 39 (2000) 1467.