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Cyclotetrameric Supersandwich Structure of a Structurally Confined C_1-Bridged Dilithiobis(cyclopentadienide)—A Case of Supramolecular LiCp-Association

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Abstract: The rigid C_1-bridged dilithiobis(cyclopentadienide) **4**, prepared by means of a fulvene route, cannot attain the usual linear $(LiCp)_2$ structure because of the angular Cp−Li−Cp confinement. Consequently, a cyclotetrameric $[Li_2(Cp-R-Cp)]_4$ supramolecular structure is observed of **4**·tmeda by X-ray diffraction, the essential structural subunits of which are very well reproduced by quantum chemical calculations.

Introduction

Depending on the substituents and the presence of donor ligands five principal structural types of LiCp compounds have been disclosed in the solid state by X-ray diffraction. Two of these, the sandwich (**A**)[1] and the inverse sandwich (**B**)[2] are charged. Then there is the ligand stabilized LiCp monomer (**C**), of which many examples have been reported.[3,4] The linear dimer of a supersandwich structure (**D**) has been documented repeatedly,[5] and consequently the (close to linear) polymeric structure (**E**) is possible and has been observed experimentally for the related Cp-potassium compounds.[6]

Bridged dilithio *μ*-alkyl- or *μ*-silyl-bis(cyclopentadienides) have become very important reagents since their reaction especially with the group 4 metal halides leads to the precursors of the homogeneous bent metallocene Ziegler-type olefin polymerization catalysts.[7] Bringing two cyclopentadienyl anions in close proximity but in a sterically rather confined arrangement should have some interesting consequences with regard to the favored structure of the dilithiobis(cyclopentadienide) system. Since the Li−Cp interaction is probably largely electrostatic and because of an otherwise unfavorable orbital interaction,[8] a bent lithiocene structure seems unlikely. This leaves only a few attractive possibilities. Among these the systems containing linear supersandwich (Li−Cp−Li−Cp) substructures represent coordinatively open units that require additional stabilization that is likely to be attained by association. Therefore, the dilithio-(*μ*-hydrocarbyl)- and -(*μ*-silyl)bis(cyclopentadienides) are good candidates to form novel organometallic structural aggregates. We have studied the association behavior of a first example of this type of a compound that indeed forms an organized oligomeric (here cyclotetrameric) structure upon crystallization.

[§] Quantum chemical calculations.

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1995.

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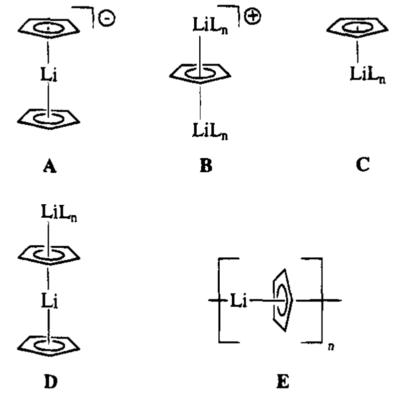
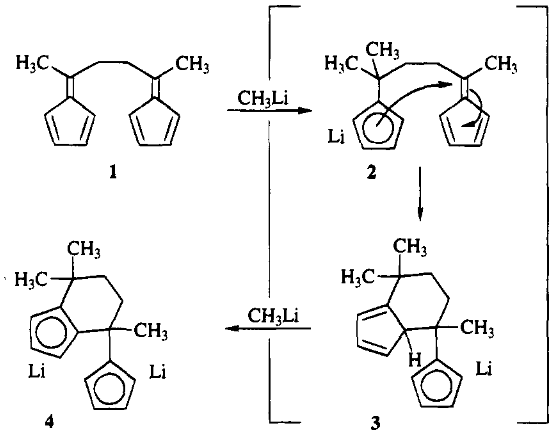
Scheme 1. Schematic Representation of LiCp Structural Types and Substructures



Scheme 2



Results and Discussion

Experimental Work. We have recently described that the 1,4-bisfulvene **1**[9] reacts readily with 2 molar equiv of methyllithium to give the rigid six-membered ring-annulated C$_1$-bridged dilithiobis(cyclopentadienide) **4**.[10] Probably methyllithium adds to a fulvene carbon producing a substituted monocyclopentadienide intermediate (**2**) that subsequently attacks the remaining fulvene functionality intramolecularly as depicted in Scheme 2 to give **3**.[11] Deprotonation by the second methyllithium equivalent then leads to the formation of **4**. The organometallic reagent was used to prepare the corresponding titanocene, zirconocene, and hafnocene dichloride complexes that were used for generating very reactive homogeneous metallocene Ziegler catalyst systems.[10,12]

We have now dissolved the dilithiobis(cyclopentadienide) **4** in toluene in the presence of tetramethylethylenediamine (tmeda). From this solution crystals were obtained that were suited for an X-ray crystal structure determination.

The dilithiobis(cyclopentadienide) crystallizes as a tetramer [**4**·(tmeda)·(toluene)$_{1.5}$]$_4$ and exhibits a cyclic structure. Thus, in the essential structural unit there are eight lithium atoms and four C$_1$-bridged bis(cyclopentadienides). All these six-membered ring-annulated C$_1$-bridged bis(cyclopentadienide) ligand systems are symmetry-equivalent, and there are two types of lithium centers in markedly different ligand environments. In the projection (see Figure 1) the eight lithium atoms form a distorted octagonal arrangement with two types of Li(1)···Li(2) separations at 5.044 and 4.048 Å. The shorter of the two is characteristic of a linear supersandwich substructure where one lithium atom (Li2) is tugged in between two η^5-cyclopentadienyl systems originating from two different C$_1$-bridged bis(cyclopentadienide) moieties and the other (Li1) is also coordinated to the tmeda molecule.

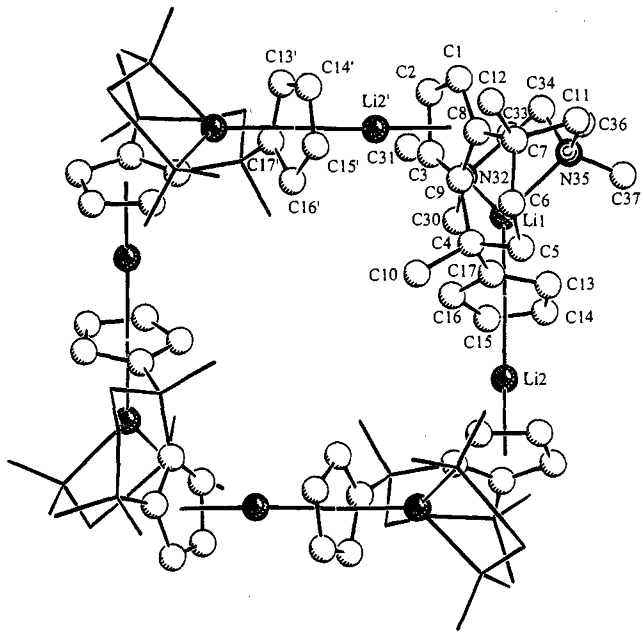


Figure 1. A view of the cyclic geometry of the 4·tmeda-tetramer.

Thus, Li2 is η^5-coordinated to the "outside" face of the tetrahydroindenyl moiety of our ligand system. The bonds of this lithium ion to the respective cyclopentadienyl methine carbon atoms are uniformly short [2.264(13) Å (Li2−C1), 2.212(12) Å (Li2−C2), 2.271(11) Å (Li2−C3)], and the bonds to the two remaining quarternary carbon centers are markedly longer at 2.348(11) Å (Li2−C9) and 2.342(12) Å (Li2−C8). Overall, the bonds between Li2 and the five carbon atoms of the other (i.e., monosubstituted) Cp-ring are longer [2.358(12) Å (Li2−C13), 2.343(11) Å (Li2−C14), 2.343(11) Å (Li2−C15), 2.356(12) Å (Li2−C16)] with the lithium to quarternary carbon distance again representing a pronounced maximum [2.379(12) Å (Li2−C17)].

The C13−C17 cyclopentadienyl ring binds equally strong to the other lithium center to complete the linear supersandwich structure[5] [2.361(12) Å (Li1−C13), 2.378(13) Å (Li−C14), 2.358(13) Å (Li1−C15), 2.318(12) Å (Li1−C16), 2.318(11) Å (Li1−C17)]. The lithium atom Li1 is also strongly coordinated to the nitrogen atoms of the tmeda ligand [2.219(11) Å (Li1-N32), 2.109(12) Å (Li1-N35)]. The coordination sphere of Li1 is completed by a weak interaction inside the "bent metallocene" wedge with carbon atoms C3 and C9 of the adjacent tetrahydroindenyl Cp-ring [2.825 Å (Li1−C3), 3.183 Å (Li1−C9)]. The distance of Li1 to the remaining three cyclopentadienide carbon atoms of this ring is very large [atom separations Li1−C1: 4.528 Å; Li1−C2: 3.798 Å; Li1−C8: 4.232 Å] and, thus, clearly outside the range of a direct bonding interaction.

The framework of eight lithium atoms of the Li$_2$(RCp$_2$) derived tetramer is not at all planar. The four Li2 atoms form,

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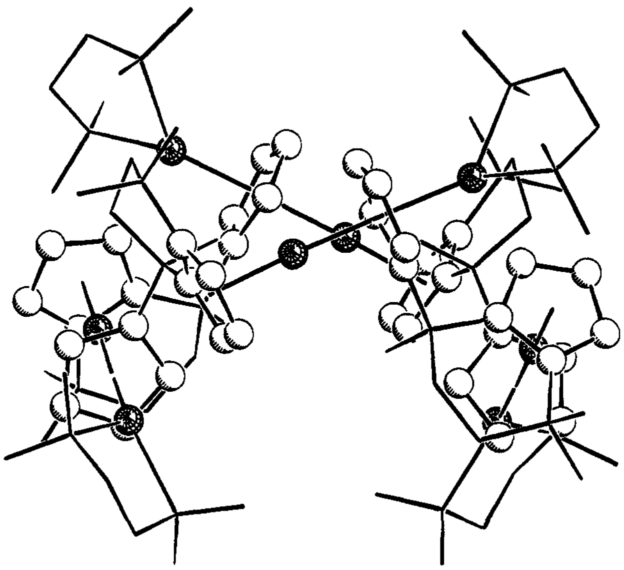

Figure 2. A side view of the tetrameric **4**·tmeda framework showing the nonplanar association of the four supersandwich substructures.

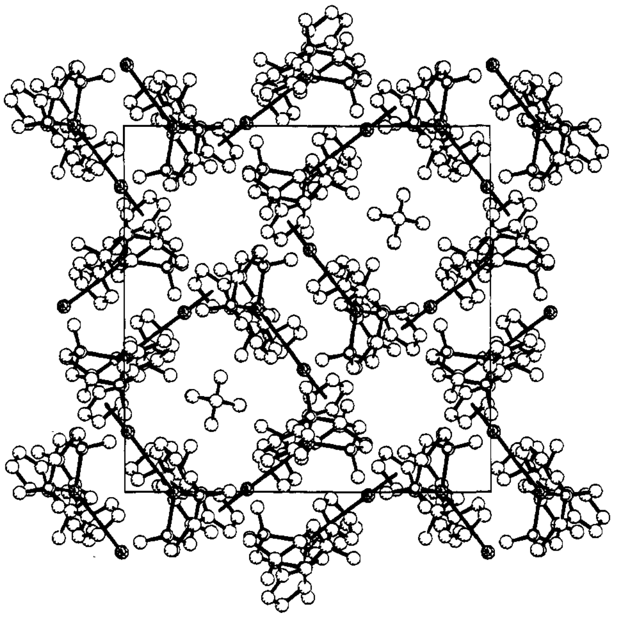

Figure 3. A projection of the molecular arrangement of the (**4**·tmeda)-tetramers; the crosslike features in the center of the organometallic ring systems each represent pairwise perpendicularly arranged toluene molecules inside the channel structure. The toluene molecules are oriented normal to the mean plane of the $(RCp)_8Li_8$ framework.

e.g., a puckered arrangement with a Li2···Li2 separation of 6.649 Å along the edges and a diagonal distance of 9.000 Å. Figure 2 provides a side view of this structural arrangement.

A view of a projection of the unit cell shows that the **4**·tmeda tetramer forms a columnar arrangement in the crystal. Two types of channels become visible in this projection: a small one is formed in places where four tetrameric units are approaching each other at their corners and a larger columnar cavity appears in the center of the stapled $Li_8(RCp_2)_4(tmeda)_4$ ring systems. The former channel is probably too small to allow for the inclusion of molecules from the surrounding, but toluene molecules have been trapped in the larger diameter channels. These are arranged perpendicularly to the mean $Li_8(RCp_2)_4(tmeda)_4$ plane but are located not inside the organometallic ring system but rather above and below it. Two of these encapsulated arenes are oriented normal to each other, with the CH_3-C_{ipso} axis being arranged parallel to the main channel orientation (i.e., on the crystallographic 4_2-axis); this results in the appearance of the cross-like features in the projection visualized in Figure 3.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for **4**·tmeda-Tetramer[a]

Li(1)−N(35)	2.109(12)	N(35)−Li(1)−N(32)	84.8(4)
Li(1)−N(32)	2.219(11)	C(8)−C(1)−C(2)	108.3(6)
Li(1)−C(16)	2.318(12)	C(3)−C(2)−C(1)	107.7(6)
Li(1)−C(17)	2.318(11)	C(2)−C(3)−C(9)	108.9(5)
Li(1)−C(15)	2.358(13)	C(9)−C(4)−C(10)	110.6(4)
Li(1)−C(13)	2.361(12)	C(9)−C(4)−C(17)	110.0(4)
Li(1)−C(14)	2.378(13)	C(10)−C(4)−C(17)	108.9(4)
Li(2)−C(2)	2.212(12)	C(9)−C(4)−C(5)	107.8(5)
Li(2)−C(1)	2.264(13)	C(10)−C(4)−C(5)	109.7(4)
Li(2)−C(3)	2.271(11)	C(17)−C(4)−C(5)	109.8(4)
Li(2)−C(8)	2.342(12)	C(6)−C(5)−C(4)	112.3(5)
Li(2)−C(14)#1	2.343(11)	C(7)−C(6)−C(5)	114.2(5)
Li(2)−C(15)#1	2.343(11)	C(6)−C(7)−C(8)	108.3(5)
Li(2)−C(9)	2.348(11)	C(6)−C(7)−C(11)	111.4(6)
Li(2)−C(16)#1	2.356(12)	C(8)−C(7)−C(11)	109.4(5)
Li(2)−C(13)#1	2.358(12)	C(6)−C(7)−C(12)	109.3(6)
Li(2)−C(17)#1	2.379(12)	C(8)−C(7)−C(12)	110.7(5)
C(1)−C(8)	1.388(8)	C(11)−C(7)−C(12)	107.6(6)
C(1)−C(2)	1.405(8)	C(1)−C(8)−C(9)	108.5(5)
C(2)−C(3)	1.392(8)	C(1)−C(8)−C(7)	128.4(6)
C(3)−C(9)	1.408(7)	C(9)−C(8)−C(7)	123.0(6)
C(4)−C(9)	1.501(7)	C(3)−C(9)−C(8)	106.6(5)
C(4)−C(10)	1.528(7)	C(3)−C(9)−C(4)	128.0(5)
C(4)−C(17)	1.541(7)	C(8)−C(9)−C(4)	125.5(5)
C(4)−C(5)	1.550(7)	C(17)−C(13)−C(14)	107.9(6)
C(5)−C(6)	1.528(8)	C(15)−C(14)−C(13)	109.0(6)
C(6)−C(7)	1.507(9)	C(14)−C(15)−C(16)	108.3(5)
C(7)−C(8)	1.527(8)	C(17)−C(16)−C(15)	107.4(5)
C(7)−C(11)	1.532(9)	C(13)−C(17)−C(16)	107.4(5)
C(7)−C(12)	1.537(8)	C(13)−C(17)−C(4)	127.5(5)
C(8)−C(9)	1.417(7)	C(16)−C(17)−C(4)	125.0(5)
C(13)−C(17)	1.395(7)	C(30)−N(32)−C(31)	108.1(6)
C(13)−C(14)	1.425(8)	C(30)−N(32)−C(33)	109.2(6)
C(14)−C(15)	1.359(8)	C(31)−N(32)−C(33)	112.4(7)
C(15)−C(16)	1.429(7)	C(30)−N(32)−Li(1)	112.5(5)
C(16)−C(17)	1.421(7)	C(31)−N(32)−Li(1)	113.3(5)
C(30)−N(32)	1.452(8)	C(33)−N(32)−Li(1)	101.3(5)
C(31)−N(32)	1.457(9)	C(34)−C(33)−N(32)	114.7(6)
N(32)−C(33)	1.459(8)	C(33)−C(34)−N(35)	113.7(6)
C(33)−C(34)	1.437(9)	C(34)−N(35)−C(37)	112.2(6)
C(34)−N(35)	1.452(8)	C(34)−N(35)−C(36)	108.9(6)
N(35)−C(37)	1.455(8)	C(37)−N(35)−C(36)	109.0(6)
N(35)−C(36)	1.463(8)	C(34)−N(35)−Li(1)	102.9(5)
		C(37)−N(35)−Li(1)	113.5(5)
		C(36)−N(35)−Li(1)	110.2(5)

[a] Symmetry transformation used to generate equivalent atoms: #1 $-y + {}^1/_2, x, -z + {}^1/_2$.

Computational Studies

Semiempirical methods (MNDO, PM3) are excellently suited to reproduce the structural features even of such complicated and unusual compounds like **4**.[13] We have optimized completely the structure of the monomer **4**·ethylenediamine by use of both methods. Especially PM3, which was recently parameterized for lithium,[14] proved to be an excellent tool for the theoretical prediction of the structural properties. Although the quantum chemical calculations simulate, of course, the gas phase behavior of the molecules, surprisingly good correlation is found with the experimentally determined X-ray data. As Table 3 demonstrates, there is good qualitative agreement between

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[13] MNDO: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907. Lithium-parameterization: Thiel, W.; Clark, T. Parameters taken from the MNDOC program Thiel, W. *QCPE Bull.* **1982**, *2*, 36.

[14] PM3: Stewart, J. J. P.; *J. Comput. Chem.* **1989**, *10*, 209, 221. Lithium-parameterization: Anders, E.; Koch, R.; Freunscht, P. *J. Comput. Chem.* **1993**, *11*, 1301. MOPAC6: Stewart, J. J. P. *QCPE* **1990**, 455.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**·tmeda-Tetramer[a]

	x	*y*	*z*	*U*(eq)
Li(1)	3644(6)	5016(6)	1198(5)	55(3)
Li(2)	1648(6)	4912(6)	2973(5)	53(3)
C(1)	2130(4)	6076(4)	2746(3)	60(2)
C(2)	1928(4)	5700(4)	2162(3)	58(2)
C(3)	2413(3)	5082(3)	2088(3)	42(2)
C(4)	3532(3)	4488(3)	2759(2)	36(2)
C(5)	4075(3)	4837(4)	3277(3)	56(2)
C(6)	3646(4)	5206(5)	3845(3)	70(2)
C(7)	3177(4)	5887(4)	3650(3)	58(2)
C(8)	2730(3)	5684(4)	3031(3)	46(2)
C(9)	2913(3)	5055(3)	2627(2)	39(2)
C(10)	3199(3)	3746(3)	3022(3)	53(2)
C(11)	3679(4)	6581(4)	3514(3)	87(3)
C(12)	2636(4)	6094(4)	4215(3)	86(3)
C(13)	4645(3)	4658(3)	1906(3)	45(2)
C(14)	4821(4)	4356(4)	1275(3)	54(2)
C(15)	4279(4)	3840(4)	1106(3)	51(2)
C(16)	3737(3)	3800(3)	1627(2)	41(2)
C(17)	3973(3)	4319(3)	2121(2)	35(1)
C(20)	5864(9)	6076(12)	3257(9)	169(8)
C(21)	5976(7)	6308(8)	2624(13)	171(8)
C(22)	6388(8)	5905(11)	2135(7)	154(5)
C(23)	6670(8)	5229(12)	2303(10)	157(6)
C(24)	6566(8)	4977(8)	2988(13)	172(9)
C(25)	6163(9)	5382(11)	3411(14)	206(12)
C(26)	6051(8)	5149(10)	4104(7)	231(10)
C(30)	3192(5)	4607(5)	−221(3)	103(3)
C(31)	2137(5)	4981(5)	412(3)	104(3)
N(32)	2942(4)	5117(3)	297(2)	66(2)
C(33)	3099(5)	5900(5)	102(4)	96(3)
C(34)	3220(5)	6416(4)	639(4)	85(2)
N(35)	3834(3)	6191(3)	1073(2)	61(2)
C(36)	3746(4)	6587(4)	1701(3)	82(2)
C(37)	4578(4)	6369(4)	801(4)	86(2)
C(41)	7500	7500	5427(7)	126(7)
C(42)	7369(6)	6856(7)	5101(5)	121(4)
C(43)	7374(5)	6838(6)	4419(5)	105(3)
C(44)	7500	7500	4064(5)	87(4)
C(45)	7500	7500	3339(6)	185(8)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Comparison of Calculated and Observed Bond Lengths in **4**·$R_2NCH_2CH_2NR_2$ (See Figure 1 for the Atom Numbering Scheme)

bond	MNDO	PM3	X-ray
Li1−C13	2.393	2.504	2.361
Li1−C14	2.547	2.441	2.378
Li1−C15	2.684	2.454	2.358
Li1−C16	2.627	2.526	2.318
Li1−C17	2.456	2.549	2.318
Li1−C3	2.385	2.633	2.825
Li1−C9	2.905	3.191	3.183
Li1−N32	2.299	2.157	2.219
Li1−N35	2.286	2.146	2.109
Li2−C1	2.212	2.347	2.264
Li2−C2	2.245	2.322	2.212
Li2−C3	2.300	2.418	2.271
Li2−C8	2.228	2.449	2.342
Li2−C9	2.303	2.507	2.348

theory and experiment. The most interesting feature certainly is the theoretical evaluation of the bonding situations for the two different lithium cations. In good agreement with experiment, the semiempirical methods supports the η^7-bonding of ethylenediamine-complexed lithium cation with only very little interaction to the other cyclopentadienyl moiety in the sense of a "bent metallocene" wedge. The other lithium cation is centered on the outside face, offering the coordination sphere for a second monomeric unit to produce the linear supersandwich structure. In general, although PM3 gives slightly longer Li−C distances for the monomer (by 0.06−0.22 Å) compared to the tetramer of the X-ray, this method provides easy and very quick access to reliable structural information of unusual organolithium compounds.

Table 4. Crystal Data and Structure Refinement for **4** · tmeda

empirical formula	$C_{23}H_{36}Li_2N_2 \cdot (C_7H_8)_{1.5}$
formula weight	492.62
temp (K)	223(2)
wavelength (Å)	1.54178
crystal system	tetragonal
space group	*P*4₂/*n* (no. 86)
a (Å)	17.592(5)
c (Å)	20.365(2)
vol (Å³)	6303(3)
Z	8
absorption coeff (mm⁻¹)	0.43
crystal size	0.5 × 0.5 × 0.3 mm
diffractometer	Enraf-Nonius CAD4
θ-range (°)	3.32−52.47
collected reflcns	3885
unique reflcns	3598
reflcns with $I \geq 2\sigma(I)$	1667
refined parameters	348
R ($I \geq 2\sigma(I)$)	0.085
wR^2 ($I \geq 2\sigma(I)$)	0.198
GoF	1.083
programs used	SHELX-86, SHELX-93, SCHAKAL-92, XP

Conclusions

The manifold of reported structures of alkali metal cyclopentadienides and related systems shows that linear arrangements of, e.g., Li−Cp−Li−Cp stacks are the preferred structural motif. This is probably due to the large electrostatic component of the Cp···metal interactions in these types of compounds. Consequently, sufficient electronic saturation of the metal is hard to achieve when this linear stacking arrangement is becoming hindered or even prohibited by the incorporation of the Cp-ring systems in constrained organic frameworks that enforce substantial deviations of hydrocarbyl bridged cyclopentadienides from a parallel arrangement of their major planes, such as it is observed in the dianionic ligand system **4**. Since a sufficient coordinative and electronic saturation of lithium is no longer reached in the typical way, even when additional ancillary ligands such as tmeda are present, novel structural types are becoming increasingly favored. In the case studied here, the novel stereoelectronic situation around lithium results in the preferred formation of the novel cyclooligomeric suprastructure. The specific Li_8(ligand)$_4$-type arrangement observed here is probably very much dependent on the special ligand system employed here which represents a very rigid C_1-bridged bis(cyclopentadienide) reagent. Other hydrocarbyl-fused Li_2-bis(cyclopentadienides), which are extremely important reagents for synthesizing the group 4 ansa-metallocene homogeneous Ziegler catalyst precursors, may exhibit variable structural details but are expected to aggregate in general in a similar way as it has here been observed for the example of **4**. It is very likely that the specific structural features of such aggregates in solution (or even in the solid state when phase transfer reactions are involved) will greatly determine the outcome of the subsequent metathesis reactions leading to the highly important ansa-metallocene systems containing the catalytically active d- or f-block elements. We have begun to actively investigate the role of the dilithiobis(cyclopentadienide) supramolecular structures on the reactivity and selectivity of the organometallic reactions of these important reagents.

Experimental Section

All reactions were carried out under Ar using Schlenk-type glassware or in a glovebox. Toluene was distilled from sodium and benzophenone, tetramethylethylenediamine (tmeda) was stirred over sodium for several days at ambient temperature and distilled under reduced pressure. The dilithiobis(cyclopentadienide) **4** was prepared like previously reported.[10] Suitable material for an X-ray crystal structure of **4**·tmeda was obtained by suspending 1.44 g (5.00 mmol) of the dilithiobis(cyclopentadienide) **4** in 50 mL of toluene. By slow addition of 0.68 mL (0.53 g, 4.50 mmol) of tmeda at room temperature an orange solution was obtained. This solution was filtered and concentrated in vacuo to a total volume of 20 mL. By storing this solution at −30 °C large yellow crystals formed within a few days. Due to the high content of solvent molecules in the crystal and a melting point below 0 °C these crystals only diffracted to relative low θ angles.

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Supporting Information Available: Details concerning the X-ray crystal structure analysis of **4**·tmeda, including complete tables of bond lengths and angles, atomic coordinates and the quantum chemical calculations (MOPAC6-Archive Entries) (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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