Oligomeric Supersandwich Structure of a Lithium Enamino-Cyclopentadienide

Vasily V. Kotov, Gerald Kehr, Roland Fröhlich, and Gerhard Erker

Organisch-Chemisches Institut der Universität Münster, Corrensstr. 40, D-48149 Münster, Germany

Reprint requests to Prof. Dr. G. Erker. E-mail: erker@uni-muenster.de

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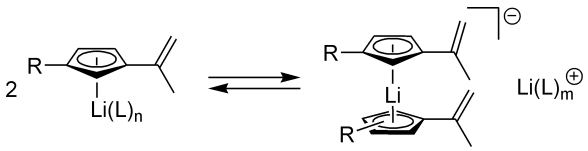
Deprotonation of 6-methyl-6-dimethylaminofulvene with a lithium amide base gave lithium (1-dimethylamino-ethenyl)cyclopentadienide. In the crystal it features a close to perfect oligomeric supersandwich structure. In contrast to related (aminomethyl-Cp)Li complexes here the enamino substituent is not directly involved in the formation of the oligomeric suprastructure.

Key words: Organolithium Compound, Lithiocene, Solid State Structure, Enamine

Introduction

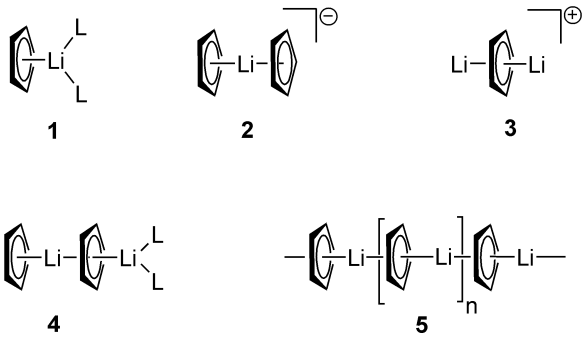
Lithium cyclopentadienides are important reagents for the synthesis of organometallic compounds. In addition they feature an interesting manifold of structural variations in solution and in the crystal [1]. Variable temperature NMR spectroscopy has revealed markedly temperature dependent equilibria between monomeric lithium cyclopentadienides and their respective lithiocene salts [2]. A typical recently described example (**1a** ⇌ **2a**) is shown in Scheme 1 [3].



1a **2a**

Scheme 1.

In the crystal, examples of various species **1** – **5** (Scheme 2) were observed for the parent LiCp system or ring-substituted derivatives, respectively [1, 4]. Of particular interest is the oligomeric structural type **5**. Such polymeric structures have often been observed in ^{R}Cp-sodium or -potassium chemistry, but less frequently for ^{R}Cp-Li examples. $[(C_5H_4SiMe_3)Li]_n$ (**5a**) features such a linear μ-(η^5–Cp^R)-type oligomeric arrangement, shown by single crystal X-ray diffraction [5, 6]. High resolution X-ray powder diffraction was used to establish the analogous polymeric $[(C_5H_5)Li]_n$ structure **5b** of the parent CpLi compound [7]. A similar oligomeric structure **5c** was recently deduced for



1 **2** **3** **4** **5**

Scheme 2.

$[(indenyl)Li]_n$ by the same method [8]. We had subsequently shown that a 2-amino-substituted indenyl lithium system adapts a similar structure **5d** in the crystal [9].

The structural situation may become more complicated when functional groups are attached to the cyclopentadienide that are able to coordinate to lithium. These donor functionalities then may become an integral part of the overall structural type observed. A typical example is a formimido-substituted lithium cyclopentadienide that was shown to form a Li^+-bridged dimeric $[(C_5H_4\text{-}CH{=}NPh)Li]_2$ structure in the crystal [10, 11]. The substituted (aminomethyl-Cp)Li derivatives **6** are especially interesting. Here the amino-groups attached to the substituent α-carbon centers are strongly coordinating to Li^+. This leads to two principal types of oligomeric structures (**6A**, **6B**, see Scheme 3) where the main chain of the organometallic oligomer is constructed by both (electrostatic) Cp-Li interactions *and* amine-Li coordination [12].

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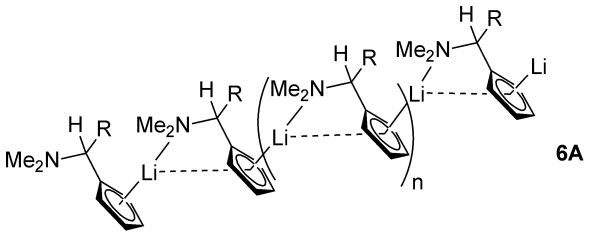
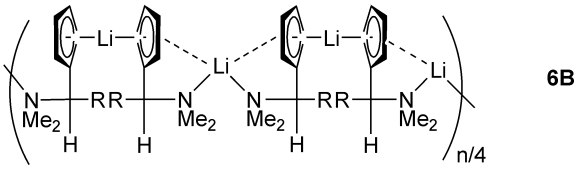


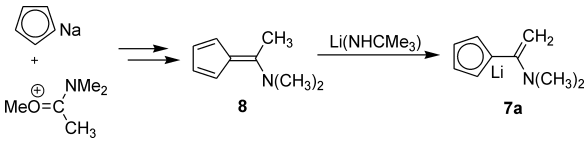


Scheme 3.

We have now varied the amino substituent bearing side chain of such systems by introducing an enamino functionality as the substituent at the Cp-ring (**7**). Whereas the topologies of the systems **6** (aminomethyl) and **7** (enamino) are related, their electronic features are quite different. This posed the question whether the enamino substituent would be involved in the construction of the oligomeric chain structure or if it would just be a structurally innocent bystander such as other alkyl or alkenyl groups. We have, therefore, synthezised a representative example (**7a**) and determined its structure in the solid state by single crystal X-ray diffraction.

Results and Discussion

The synthesis of the (enamino-Cp)Li derivative **7a** was carried out by means of the fulvene route [13, 14]. For this purpose 6-methyl-6-(dimethyl-amino)pentafulvene (**8**) was prepared by treatment of sodium cyclopentadienide with O-methylated dimethylacetamide, as described by Hafner *et al.* [15]. The substituted fulvene **8** was then C-deprotonated by treatment with the base Li(NH*t*Bu), generated *in situ* by the reaction of *tert*-butylamine with a stoichiometric amount of *n*-butyllithium. The deprotonation reaction gave the (enamino-Cp)Li derivative **7a** in *ca.* 95% yield as a yellowish solid (Scheme 4). In [D_8]-THF solution the compound **7a** features a typical ^{1}H NMR AA′BB′ pattern of the C_5H_4 protons and a pair of $=CH_2$ singlets at $\delta = 3.77$ and 3.34 in addition to a singlet (6H) of the $-N(CH_3)_2$ methyl protons. The corresponding ^{13}C NMR signal for NMe_2 is found at $\delta = 41.8$. The C_5H_4 ring carbons give rise to ^{13}C NMR resonances at



Scheme 4.

$\delta = 118.5$, 104.1 and 103.1 and the enamino C=CH_2 double bond carbon NMR signals occur at $\delta = 157.9$ and 80.2.

Single crystals of compound **7a** were obtained by crystallization from a THF/pentane mixture. The X-ray crystal structure analysis shows the presence of an oligomeric supersandwich structure in which the Li atoms are almost ideally connecting pairs of the substituted Cp-anion ring systems. The Li-C(Cp) distances to the neighboring 10 carbon atoms of the covering ^{R}Cp units are found in the narrow range of 2.248(5) to 2.408(5) Å. Within each ^{R}Cp-Li coordination sphere the Cp-rings are slightly shifted from an ideally symmetrical bonding situation. This small structural effect seems to be caused by the attached substituent. It turns out that within the Li-(C1 to C5) unit, the Li-C1 distance (*i. e.* to the carbon center bearing the enamino substituent) is slightly longer at 2.408(5) Å than the adjacent Li-C2 (2.321(4) Å) and Li-C5 (2.377(4) Å) distances followed by slightly shorter Li-C3 (2.248(5) Å) and Li-C4 (2.288(4) Å) distances. A similar effect is observed for the adjacent Li-(C1$^{\#}$ to C5$^{\#}$) coordination. However, the variation between these Li-C(Cp) distances is small. The oligomeric [(enamino-Cp)Li]$_n$ chain of **7a** is close to an undisturbed periodically repeating supersandwich structural situation (Fig. 1).

Each Cp-ring at the repeating Li[C_5H_4-C(NMe_2)=CH_2] subunit has a –C(NMe_2)=CH_2 substituent bonded to it (C1-C6: 1.486(3) Å, C6-N1: 1.406(3) Å, N1-C8: 1.457(3) Å, N1-C9: 1.459(3) Å). The core of the enamino substituent is planar (sum of bond angles at C6: 359.8°). However, the sum of bond angles at N1 is slightly smaller (344.4°). Such a slight pyramidalization at nitrogen is typical of enamine structures [16]. Accordingly, the angle between the C1-C6-C7 and C8-N1-C9 planes amounts to 41.1°.

Our study has shown that the oligomeric supersandwich structure of [CpLi]$_n$ systems in the crystal is maintained upon formal attachment of the –C(NMe_2)=CH_2 enamino substituent. In the solid state there is no evidence for any direct interaction of this electron-rich functional group with the Li^+ cations. Thus it seems that structurally the enam-

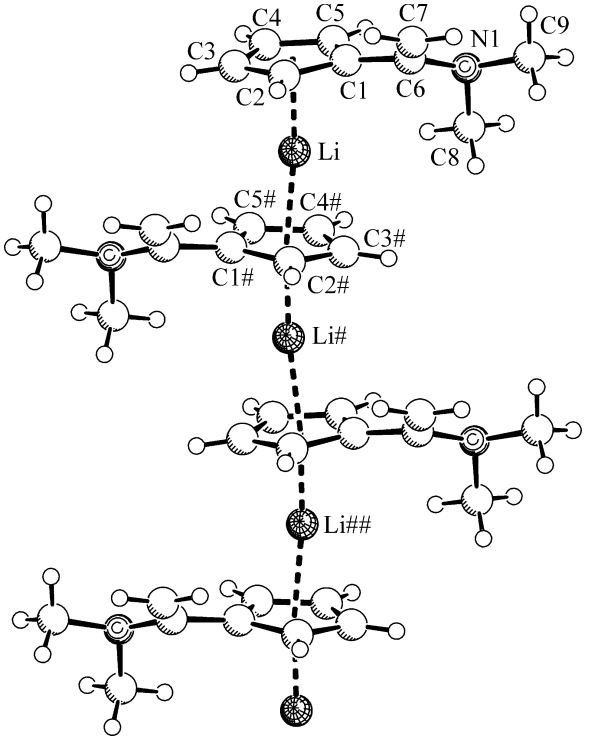


Fig. 1. A view of repeating parts of the oligomeric supersandwich chain structure of **7a**. Selected bond lengths (Å) and angles (°): C1-C2 1.415(3), C1-C5 1.418(3), C2-C3 1.411(3), C3-C4 1.405(3), C4-C5 1.405(3), Li-C1$^{\#}$ 2.345(4), Li-C2$^{\#}$2.318(4), Li-C3$^{\#}$2.293(5), Li-C4$^{\#}$2.291(5), Li-C5$^{\#}$2.326(5), Li-Li$^{\#}$-Li$^{\#\#}$ 174.3, C7-C6-N1 123.0(2), C7-C6-C1 120.5(2), N1-C6-C1 116.3(2), C6-N1-C8 117.6(2), C6-N1-C9 116.2(2), C8-N1-C9 110.6(2), dihedral angles (°) C1-C6-N1-C8 −53.5(2)°, C1-C6-N1-C9 172.1(2)°, C7-C6-N1-C8 132.1(2)°, C7-C6-N1-C9 −2.4(3)° C5-C1-C6-N1 42.3(3)°, C5-C1-C6-C7 −37.1(2)°, for additional values see the text.

ino substituent in **7a** behaves very different from the dimethylamino-methyl side-chains in the systems **6** (see above) [10], which are actively involved in the construction of the respective supramolecular structures by $Me_2N \rightarrow Li^+$ coordination. There seems to be a strict borderline separating the –CHR-NMe_2 and the –C(=CH_2)-NMe_2 substituents in their ability to serve as structural building blocks in substituted Cp-Li chemistry according to their different coordinative abilities.

Experimental Section

Reactions with organometallic compounds were carried out under argon in Schlenk type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. The following instruments were used for spectroscopic and physical characterization: Bruker AC 200P and AMX 400 NMR spectrometers, Varian 3100 FT-IR Excalibur Series; elemental analyses: Vario El III Mikro; melting point: DSC 2010, TA-Instruments.

X-ray crystal structure analysis

The data set was collected with a Nonius Kappa CCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN [17], absorption correction SORTAV [18], structure solution SHELXS-97 [19], structure refinement SHELXL-97 [20], graphics SCHAKAL [21]. CCDC 611791 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

*Preparation of lithium (1-dimethylaminoethenyl)cyclopentadienide (**7a**)*

A solution of LiN(H)^{t}Bu, generated by treatment of 4.0 mL (37.0 mmol) of *tert*-butylamine with 23.1 mL of a 1.6 M solution of *n*-butyllithium (37.0 mmol) in hexane, was added dropwise with stirring to a solution of 5.0 g (37.0 mmol) of 6-methyl-6-dimethylaminofulvene (**8**) [14, 15] in THF (50 mL) at r. t.. The reaction mixture was stirred for 48 h at ambient temperature. Solvent and volatiles were then removed *in vacuo*. The remaining yellow solid was washed with pentane (3 × 30 mL) and dried *in vacuo* to yield 4.9 g (95%) of **7a**. DSC: M. p. 87 °C, 207 °C (decomp.). – IR (KBr): ν = 3190, 3089, 3071, 3005, 2976, 2938, 2836, 2788, 1818, 1746, 1715, 1611, 1572, 1482, 1448, 1359, 1338, 1223, 1149, 1122, 1102, 1054, 1030, 1004, 922, 902, 874, 843, 813, 761 cm^{-1}. – ^{1}H NMR (300 MHz, [D$_8$]-THF, 300 K): δ = 5.66, 5.45 (2 × m, 2 × 2H, C_5H_4), 3.77, 3.34 (2 × s, 2 × 1H, =CH_2), 2.45 (s, 6H, N(CH_3)$_2$). – ^{13}C{^{1}H} NMR (75.5 MHz, [D$_8$]-THF, 300 K): δ = 157.9 (*C*=CH_2), 118.5, 104.1, 103.1 (C_5H_4), 80.2 (=*C*H_2), 41.8 (N(*C*H_3)$_2$). – $C_9H_{12}LiN$ (141.1): calcd. C 76.59, H 8.57, N 9.92; found C 74.62, H 8.63, N 9.66.

*X-ray crystal structure analysis of **7a***

Single crystals were obtained from a THF/pentane mixture, formula $C_9H_{12}LiN$, M = 141.14, yellow crystal 0.25 × 0.20 × 0.15 mm, monoclinic space group *Cc* (no. 9), a = 6.751(1), b = 17.244(3), c = 7.837(1) Å, β = 114.63(1)°, V = 829.3(2) Å^3, ρ_{calc} = 1.130 g cm^{-3}, μ = 0.064 mm^{-1}, empirical absorption correction ($0.984 \leq T \leq 0.991$), Z = 4, λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 3637 reflections collected ($\pm h, \pm k, \pm l$), [$(\sin\theta)/\lambda$] = 0.67 Å^{-1}, 1853

independent ($R_{\text{int}} = 0.052$) and 1219 observed reflections [$I \geq 2I$)], 103 refined parameters, $R = 0.049$, $wR^2 = 0.111$, max. residual electron density 0.19 (−0.16) e Å^{-3}; hydrogen atom positions were calculated and refined as riding atoms.

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