# 2-[Ethyl-(2-methallyl)amino]indenyllithium: Structural Characterization of a Base-Free Oligomeric Supersandwich Indenyllithium Compound

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Treatment of the enamine **2**, formed by condensation of 2-indanone and ethyl(2-methallyl)amine, with *n*-butyllithium yields 2-[ethyl(2-methallyl)amino]indenyllithium (**3**), whose structure was determined by X-ray single crystal diffraction. Complex **3** exhibits an oligomeric supersandwich structure in the solid state, characterized by a linear string of alternating μ-$\eta^5$:$\eta^5$-indenyl anion and lithium cation moieties along which the substituents are found attached in a helical conformational arrangement.

## Introduction

The alkali metal cyclopentadienides and their benzo-anellated analogues are important reagents in organic and organometallic synthesis, but have also attracted a great deal of interest in themselves due to their unique structural properties. The high electrostatic component of the carbon−alkali metal bond[1] has made a variety of specific structural arrangements possible for the family of the $^{R}CpM^{I}$ systems, ranging from neutral ($^{R}Cp$)$ML_n$ monomers to cationic [$M-^{R}Cp-M^+$, "inverse sandwich"] and anionic [$^{R}Cp-M-^{R}Cp^-$, sandwich] arrangements, and to neutral-ligand-capped dimeric [$^{R}Cp-M-^{R}Cp-ML_n$] or oligomeric [$^{R}Cp-M-^{R}Cp-M$]$_n$ "supersandwich" structures.[2] The latter polymers are frequently encountered in $^{R}Cp$ sodium or potassium chemistry, but so far the lithium analogues have seldom been unambiguously characterized. The first example, [$(C_5H_4SiMe_3)Li$]$_n$, was only recently described,[3−6] and its structure was solved by a single crystal X-ray diffraction analysis. Oligomeric (CpLi)$_n$ was recently characterized by high resolution X-ray powder diffraction.[7] The same technique was used for the determination of the oligomeric supersandwich structure of ($\eta^5$-indenyl-Li)$_n$ in the solid state [with Li-indenyl five-membered ring distances ranging between 2.304(3) Å and 2.350(3) Å].[8] Oligomeric (indenyl-Li)$_n$, characterized by X-ray powder diffraction, exhibits local internal $C_s$-symmetry. We describe here the structure of a related (2-aminoindenyl)Li reagent (**3**), whose oligomeric supersandwich structure was determined by single crystal X-ray diffraction.

## Results and Discussion

### Preparation and Structure of the 2-[Ethyl(2-methallyl)-amino]indenyllithium Oligomer

The title compound **3** was prepared in the following way: 2-indanone was treated with a ca. threefold excess of ethyl(2-methallyl)amine in toluene in the presence of 3 Å molecular sieves to yield the corresponding enamine **2** (85% isolated).[9] Treatment of **2** with *n*-butyllithium in toluene/hexane resulted in the formation of the amino-substituted indenyllithium compound **3** in almost quantitative yield. The NMR spectra of **3** in [D$_8$]THF solution show the signals of a conformationally averaged, 2-substituted indenyl ligand (1-/3-H NMR signal at $\delta = 5.35$; arene resonances at $\delta = 6.35$ and 7.05). Single crystals of this specifically substituted indenyllithium example were obtained by slowly concentrating a solution of **3** in a mixture of toluene/ether (90:10) in a stream of argon at −20 °C during 48 h. The obtained single crystals of **3** were free of the donor ligand and suitable for characterization by an X-ray crystal structure analysis.

In the crystal the indenyllithium compound **3** adopts a polymeric supersandwich structure composed of alternating $\eta^5$-(2-aminoindenyl) units and intercalating lithium atoms. There are three crystallographically independent Li(R$_2$N-indenyl) subunits present in the solid, which represent chemically equivalent moieties. The planes of the individual 2-[ethyl(2-methallyl)amino]indenyl units are oriented almost parallel to each other [angles between the individual Cp planes: 15.9° ("Cp1"/"Cp21"), 16.6° ("Cp21"/"Cp41"), and 10.3° ("Cp41"/"Cp1")]. The lithium atoms are symmetrically $\eta^5$-coordinated from either side of the indenyl five-membered ring systems. Within all three independent subunits the minimum/maximum Li−C indenyl values amount to 2.237(7) Å (Li3−C1$^{\#}$) and 2.389(7) Å (Li1−C8). The Li1−C1,2,7−9(av.) values, averaged over the three inde-

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[++] NMR spectroscopy

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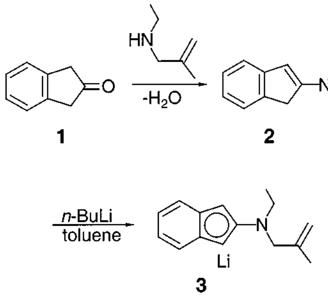
pendent molecules, are within a narrow range between 2.288(7) and 2.321(7) Å; the corresponding Li1−C21,22,27−29(av.) values are found between 2.284(7) and 2.313(7) Å. The overall averaged Li−C bond lengths to either side of the Cp sections of the indenyl ligands in the supersandwich structure amount to 2.305 Å [Σ Li1−C1,2,7−9(av.)/5] and 2.297 Å [Σ Li1−C21,22,27−29(av.)/5], which illustrates the symmetrical bonding of the lithium atoms between adjacent $\eta^5$-indenyl ligands along the oligomeric chain in the crystal of **3** (see Figure 1). Both these averaged Li−C(av.) distances of **3** are smaller than the respective value determined in the recent X-ray powder diffraction study of (indenyl-Li)$_n$ (2.320 Å).[8] The Li−C(av.) values found for **3** are close to the average Li−C(Cp) values obtained from the X-ray powder diffraction study of the parent (CpLi)$_n$ oligomer (2.307 Å).[7]

The framework of the 2-[ethyl(2-methallyl)amino]indenyl ligand in **3** is completely planar (sum of averaged C−C−C bond angles inside the five-membered ring: 539.9°; inside the six-membered ring: 720.0°). The C−C bond lengths inside the five-membered ring are in a narrow range between 1.439(5) Å (C2−C7) and 1.411(5) (C8−C9)/1.413(4) (C1−C9). The pronounced contact of the lithium atoms to all five carbon atoms of the indenyl five-membered ring has a marked influence on the bonding features of the anellated planar arene system, which exhibits a marked bond alternation: the C3−C4(av.) [1.364(5) Å] and C5−C6(av.) [1.367(5) Å] bonds (see Figure 1) are noticeably shorter than the adjacent C4−C5(av.) [1.400(5) Å] bonds, as expected for an overall bonding situation of **3** as indicated in Scheme 1.

The coordination geometry of the nitrogen atom N10 in **3** is very close to trigonal planar (sum of C−N−C bond angles: 356.7°), and the amino-substituent is oriented in the central ligand plane. The C9−N10(av.) linkage is short {1.387(4) Å, the adjacent N10−C11(av.) [1.450(4) Å] and N10−C13(av.) [1.444(5) Å] bonds being much longer}, which indicates an enamine-like interaction at the aminoin-



Scheme 1

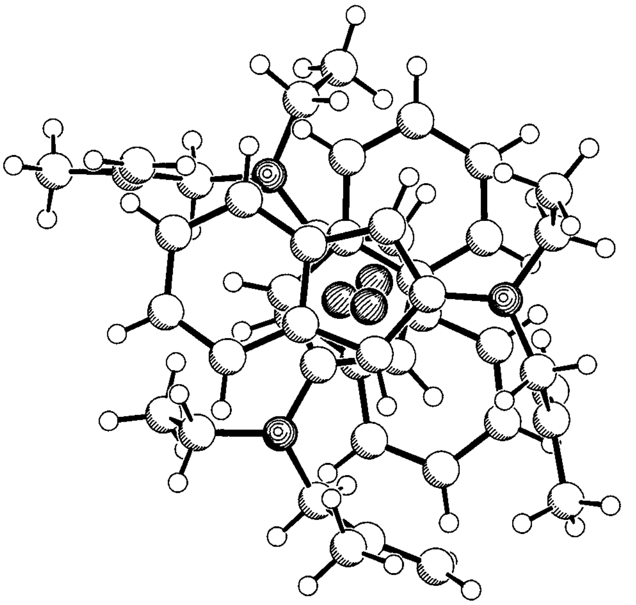


Figure 2. Top view of the arrangement of the three independent molecules of **3**

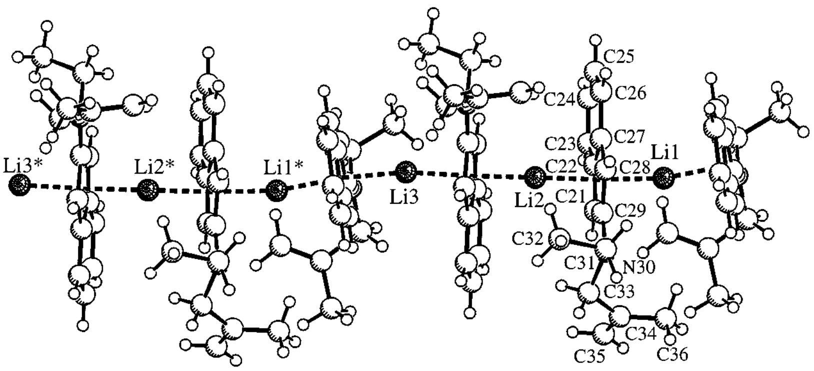


Figure 1. Side view of the oligomeric supersandwich chain of **3** with unsymmetrical atom numbering scheme, containing two pairs of the set of three independent monomeric subunits found in the crystal; averaged (av.) bond lengths (Å) and angles (°): Li1−C1(av.) = (Li1−C1 + Li2−C21 + Li3−C41)/3 = 2.289(7), Li1−C2(av.) 2.288(7), Li1−C7(av.) 2.317(7), Li1−C8(av.) 2.321(7), Li1−C9(av.) 2.308(7), Li1−C21(av.) 2.285(7), Li1−C22(av.) 2.284(7), Li1−C27(av.) 2.297(7), Li1−C28(av.) 2.313(7), Li1−C29(av.) 2.306(7), C1−C2(av.) 1.424(5), C1−C9 1.413(4), C2−C7(av.) 1.439(5), C7−C8(av.) 1.423(5), C8−C9(av.) 1.411(5), C2−C3(av.) 1.412(5), C3−C4(av.) 1.364(5), C4−C5(av.) 1.400(5), C5−C6(av.) 1.367(5), C6−C7(av.) 1.406(5), C9−N10(av.) 1.387(4), N10−C11(av.) 1.450(4), C11−C12(av.) 1.523(6), N10−C13(av.) 1.444(5), C13−C14(av.) 1.480(6), C14−C15(av.) 1.330(6); C9−C1−C2(av.) 108.2(3), C1−C2−C3(av.) 133.1(3), C1−C2−C7(av.) 107.5(3), C3−C2−C7(av.) 119.3(3), C2−C3−C4(av.) 119.4(3), C3−C4−C5(av.) 121.3(4), C4−C5−C6(av.) 121.3(4), C5−C6−C7(av.) 119.5(4), C6−C7−C8(av.) 133.5(3), C6−C7−C2(av.) 119.2(3), C2−C7−C8(av.) 107.3(3), C7−C8−C9(av.) 108.5(3), C8−C9−C1(av.) 108.4(3), C8−C9−N10(av.) 125.8(3), C1−C9−N10(av.) 125.7(3), C9−N10−C11(av.) 119.8(3), C9−N10−C13(av.) 119.2(3), C11−N10−C13(av.) 117.7(3), N10−C13−C14(av.) 115.2(4), C13−C14−C15(av.) 120.8(4), C13−C14−C16(av.) 117.0(3), C15−C14−C16(av.) 122.1(6)

denyl unit,[10] probably resulting in an increased electron density at carbon inside this anionic ligand system.

The conformational arrangement of the indenyl anions along the $[-\mathrm{Li}-\mathrm{Cp(centroid)}-]_n$ vector is such that the amino substituents are arranged almost ideally staggered along the chain (see Figure 2) which is characterized by dihedral angles of close to 120° between the corresponding N−C(Cp) vectors. There are subtle differences in the conformational arrangement of the rather large methallyl substituents at the three independent Li−2-[ethyl(2−methallyl)amino]indenyl subunits [one $-CH_2-C(CH_3)=CH_2$ group pointing "up", one "down" and one being arranged in the ligand plane] that lead to the observed marginal deviation of the overall chain from ideal linearity (see Figure 1).

## Conclusions

We conclude that compound **3** seems to represent the first example of a base-free oligomeric ($\mu$-$\eta^5$:$\eta^5$-indenyl) lithium supersandwich system that was characterized by an X-ray single crystal structure analysis. The amino-functionalized ($\eta^5$-indenyl)Li structure **(3)** exhibits shorter bonds between the lithium atom and the carbon atoms of the indenyl five-membered ring than in the recent high resolution X-ray powder diffraction analysis of the ($\eta^5$-indenyl-Li) structure.[8] Like the parent $(\text{indenyl-Li})_n$, the amino-substituted compound **3** exhibits an organometallic oligomeric structure in the solid state. The 2-[ethyl(2-methallyl)amino]indenyllithium polymer **(3)** is characterized by a regularly alternating arrangement of $\eta^5$-aminoindenyl anion moieties and lithium cations, probably formed by dominant electrostatic metal−carbon interactions. The helical conformational arrangement of the substituents at the resulting oligomeric chain indicates that such systems possess well-defined stereochemical features in the crystal. The use of such substituted indenyllithium reagents is currently being studied in our laboratory.

## Experimental Section

All reactions were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for the NMR spectroscopic characterization) were dried and distilled under argon prior to use. For additional general information see ref.[4] and ref.[5a] NMR experiments were carried out on a Varian Unity Plus 600 NMR spectrometer. The $^1$H and $^{13}$C NMR assignments were confirmed by GCOSY, GHSQC, GHMBC and DPFGSE-NOE experiments. The $\delta(^{15}N)$ determination was performed by indirect detection by the $^1$H,$^{15}$N-GHMBC experiment [preparation delay: $1/(2J) = 0.1$ s)]. Compound **2** was synthesized in analogy to a literature method.[9]

**Preparation of 2-[Ethyl(2-methallyl)amino]indene (2):** 2-Indanone (**1**, 3.2 g, 24.2 mmol) was added to a stirred suspension (3 g) of activated 3 Å molecular sieves in 40 mL of toluene. Ethyl(2-methallyl)amine (7.02 g, 72.6 mmol) was added, and the reaction mixture was stirred for 1 day at 70 °C. The mixture was filtered and the remaining molecular sieves washed with toluene (20 mL). Volatiles were removed from the combined organic solutions in vacuo to yield **2** as a liquid (4.31 g, 85%). HRMS (ESI): calcd. for $C_{15}H_{19}NH^+$: $m/z = 214.1596$; found $m/z = 214.1572$. − $^1$H NMR (599.1 MHz, [D$_8$]toluene, 298 K): indene: $\delta = 7.04$ (dd, 1 H, 5-H), 7.01 (d, 1 H, 7-H), 6.93 (d, 1 H, 4-H), 6.76 (dd, 1 H, 6-H), 5.19 (s, 1 H, 3-H), 3.00 (s, 2 H, 1-H); 2-methallyl: $\delta = 4.66$ (s, 2 H, $=CH_2$), 3.28 (s, 2 H, $CH_2$), 1.43 (s, 3 H, $CH_3$); ethyl: $\delta = 2.87$ (q, 2 H, $CH_2$), 0.85 (t, 3 H, $CH_3$). − $^{13}$C NMR (150.7 MHz, [D$_8$]toluene, 298 K): indene: $\delta = 156.0$ (C2), 148.7 (C3a), 136.8 (C7a), 126.9 (C5), 122.8 (C7), 119.9 (C6), 116.9 (C4), 96.6 (C3); 2-methallyl: $\delta =$ 142.0 (quat.-C), 111.3 ($=CH_2$), 56.1 ($CH_2$), 56.1 ($CH_2$), 19.9 ($CH_3$); ethyl: $\delta = 45.1$ ($CH_2$), 12.0 ($CH_3$). − $^{15}$N NMR (60.7 MHz, [D$_8$]toluene, 298 K): $\delta = -306$.

**Preparation of 2-[Ethyl(2-methallyl)amino]indenyllithium (3):** *n*-Butyllithium (17.0 mmol, 9.8 mL of a 1.75 M solution in hexane) was slowly added at −78 °C to a stirred solution of 2-[ethyl(2-methallyl)amino]indene (**2**, 3.46 g, 16 mmol) in toluene (30 mL). The reaction mixture was allowed to warm to room temperature and then stirred for 16 h. The resulting solid was recovered from the suspension by filtration, washed with pentane (2 × 10 mL) and dried in vacuo to yield 3.50 g (98%) of **3** as a white solid. $^1$H NMR (599.1 MHz, [D$_8$]THF, 298 K): indene: $\delta = 7.02$ (m, 2 H, 4-H, 7-H), 6.31 (m, 2 H, 5-H, 6-H), 5.33 (s, 2 H, 3 H); 2-methallyl: $\delta =$ 4.91 (s, 1 H) and 4.76 (s, 1 H, $=CH_2$), 3.74 (s, 2 H, $CH_2$), 1.73 (s, 3 H, $CH_3$); ethyl: $\delta = 3.26$ (2 H, $CH_2$), 1.08 (t, 3 H, $CH_3$). − $^{13}$C NMR (150.7 MHz, [D$_8$]THF, 298 K): indene: $\delta = 151.1$ (C2), 131.5 (C3a, C7a), 119.2 (C4, C7), 115.5 (C5, C6), 80.5 (C1, C3); 2-methallyl: $\delta = 148.7$ (quat.-C), 113.5 ($=CH_2$), 61.3 ($CH_2$) 23.5 ($CH_3$); ethyl: $\delta = 48.5$ ($CH_2$), 14.8 ($CH_3$). − $^{15}$N NMR (60.7 MHz, [D$_8$]THF, 298 K): $\delta = -326$.

**X-ray Crystal Structure Analysis of 3:** Single crystals were obtained from a toluene/ether (9:1) solution, that was concentrated under argon at −20 °C. $C_{15}H_{18}NLi$, $M = 219.24$, $a = 16.447(1)$, $b =$ 11.611(1), $c = 21.706(1)$ Å, $\beta = 101.01(3)°$, $V = 4068.8(5)$ Å$^3$, $\mu =$ 0.61 cm$^{-1}$, $Z = 12$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda =$ 0.71073 Å, $T = 198$ K, 9655 reflections collected ($\pm h$, $\pm k$, $\pm l$), 5336 independent ($R_{\mathrm{int}} = 0.075$) and 2864 observed reflections [$I \geq 2\,\sigma(I)$], $R = 0.065$, $wR^2 = 0.139$. The data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33−37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421−426), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997). − Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-144456. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

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