

Supporting Information

for

Elucidation of LiX Salt-Effect in Lithiumorganic Reagents

*Daniel Stern, Nils Finkelmeier and Dietmar Stalke**

Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37075 Göttingen, Germany

* To whom correspondence should be addressed. Fax: +49-551-393459.

Email: dstalke@chemie.uni-goettingen.de

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(1) Experimental details and physical data

All manipulations were carried out under dry nitrogen inert gas atmosphere by using modified Schlenk techniques^[S1] or in an argon drybox. THF, diethylether and DME were freshly distilled from sodium-potassium alloy prior to use. The employed reactant 9,10-dibromoanthracene was synthesized according to literature procedures.^[S2] NMR spectra were recorded on Bruker Avance 300, 400 or 500 spectrometer. The chemical shifts δ are given in ppm with tetramethylsilane (^1H and ^{13}C) as external standard. Elemental analyses were performed at the Analytisches Labor des Institutes für Anorganische Chemie der Georg-August-Universität, Göttingen.

9,10-Dibromoanthracene: A solution of 1.0 g (5.61 mmol) anthracene in 20 mL CHCl_3 was treated at rt with two eq. Br_2 (0.58 mL, 11.32 mmol) in 10 mL of CHCl_3 . After stirring for additional four h the solvent was removed i. vac. and the crude yellow reaction product was purified by re-crystallization from CH_2Cl_2 yielding the product as yellow needles; Yield: 2.39g (98%); $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 8.62-8.56 (m, 4H, $\text{H}_{1,4,5,8}$), 7.66-7.61 (m, 4H, $\text{H}_{2,3,6,7}$); $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ = 131.06 (s, 4C, $\text{C}_{4a,8a,9a,10a}$), 128.28 (s, 4C, $\text{C}_{1,4,5,8}$), 127.47 (s, 4C, $\text{C}_{2,3,6,7}$), 123.53 (s, 2C, $\text{C}_{9,10}$). EI-MS: m/z (%): 335.9 (100) $[\text{M}]^+$, 254.9/256.9 (9/9) $[\text{M} - \text{Br}]^+$, 176 (61) $[\text{M} - 2 \text{Br}]^+$. CH, found. (calc.) [%]: C 49.69 (50.04), H 2.26 (2.40).

9-Bromo-10-lithioanthracene: A suspension of 10 mmol of dibromo anthracene in 80 mL diethyl ether was cooled to $-15\text{ }^\circ\text{C}$ and over 30 min exactly 10 mmol of a 2.25 M *n*BuLi-solution in hexane was added drop wise. The obtained clear orange solution was stirred for 30 min at $0\text{ }^\circ\text{C}$ and then the solvent was reduced in vacuo to one third of the original volume. Subsequently, the solution was cooled to $-78\text{ }^\circ\text{C}$ and the solid formed during the cooling process was isolated by filtration, washed with 5-10 mL of cold hexane and dried in vacuo for 10 min.

$[\text{Br}(\text{C}_{14}\text{H}_8)\text{Li} \cdot \{\text{thf}\}_2]$ (1): 0.1 mmol of 9-Bromo-10-lithioanthracene were dissolved in 10 mL of diethyl ether and cooled to $-15\text{ }^\circ\text{C}$. Four equivalents of cold THF were added slowly and afterwards insoluble residue was removed by filtration. The solution was stored at $-25\text{ }^\circ\text{C}$ for crystallization and after ca. 24 h crystals that were suitable for diffraction experiments were obtained.

$[\text{Br}(\text{C}_{14}\text{H}_8)\text{Li} \cdot \{\text{dme}\}]_2$ (2): 0.1 mmol of 9-Bromo-10-lithioanthracene were dissolved in 10 mL of diethyl ether and cooled to $-15\text{ }^\circ\text{C}$. Two equivalents of cold DME were added slowly and afterwards insoluble residue was removed by filtration. The solution was stored at $-25\text{ }^\circ\text{C}$ for crystallization and after ca. 24 h crystals that were suitable for diffraction experiments were obtained.

$[\text{Br}(\text{C}_{14}\text{H}_8)\text{Li} \cdot \text{LiBr} \cdot \{\text{thf}\}_4]$ (3): 0.1 mmol of 9-Bromo-10-lithioanthracene were dissolved in 10 mL of diethyl ether and cooled to $-15\text{ }^\circ\text{C}$. One equivalent of LiBr (as a standard solution in THF) was added slowly. Afterwards insoluble residue was removed by filtration. The solution was stored at $-25\text{ }^\circ\text{C}$ for crystallization and after ca. 24 h crystals that were suitable for diffraction experiments were obtained.

[Br(C₁₄H₈)Li • LiBr • {dme}₂] (4): 0.1 mmol of 9-Bromo-10-lithiumanthracene were dissolved in 10 mL of diethyl ether and cooled to -15 °C. One equivalent of LiBr (as a standard solution in THF) was added slowly. Then two equivalents of DME were added to the solution. Afterwards insoluble residue was removed by filtration. The solution was stored at -25 °C for crystallization and after ca. 24 h crystals that were suitable for diffraction experiments were obtained.

Due to poor solubility in non-donating NMR solvents such as benzene d-6 or toluene d-8, acquisition of NMR data was not successful for **1** to **4**. Although the solubility of **1** to **4** in THF d-8 is good, this solvent is not suitable for acquisition of NMR data which resemble the solid state structures. In the presence of an excess amount of strongly donating solvents such as THF, the dimeric structures observed in the solid state is not retained and the AnLiLiX integrity is not maintained. Therefore only non-donating NMR solvents would lead to sensible results resembling the solid state structure.

Elemental analyses of **1** to **4** were also unsuccessful. Due to high reactivity towards aerial oxygen, no satisfying results were achieved for **1** and **2**. Although **3** and **4** show greater stability towards oxygen, the loosely bound donor molecules which evaporate during the analytical process hampered the acquisition of reliable CHN analytical data.

(2) X-ray crystallography.

Single crystals were selected from the Schlenk flasks under argon atmosphere and covered with perfluorated polyether oil on a microscope slide, which was cooled with a nitrogen gas flow using the X-TEMP2.^[S3] An appropriate crystals were selected using a polarize microscope, mounted on the tip of a glass fibre, fixed to a goniometer head and shock cooled by the crystal cooling device. For **1**, **2** and **3** data were collected on a Bruker SMART-APEXII Quazar diffractometer with D8 goniometer (100 K, Mo K_α radiation, λ = 71.073 pm; INCOATEC Quazar mirror optics),^[S4] for **4** data was collected on a Bruker APEXII Ultra diffractometer with D8 goniometer (100 K Mo K_α radiation, λ = 71.073 pm; INCOATEC Helios mirror optics). The data were integrated with SAINT,^[S5] and an empirical absorption correction (SADABS) was applied.^[S6] The structures were solved by direct methods (SHELXS) and refined on F² using the full-matrix least-squares methods of SHELXL.^[S7] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to sp² (sp³) carbon atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 (1.5) times the U_{eq} value of the parent carbon atom. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Centre, the CCDC numbers are listed in Table S1. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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(3) Table S1. Crystallographic data for the structural analyses of compounds **1**, **2**, **3** and **4**.

	1	2	3	4
empirical formula	C ₄₄ H ₄₈ Br ₂ Li ₂ O ₄	C ₃₆ H ₃₆ Br ₂ Li ₂ O ₄	C ₈₂ H ₁₀₄ Br ₅ Li ₅ O ₁₀	C ₂₂ H _{28.25} Br _{1.75} Li ₂ O ₄
CCDC no.	766244	766245	766246	766247
formula weight	814.52	706.35	1683.90	510.22
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	P $\bar{1}$	P2 ₁ /n	P $\bar{1}$	C ₂ /c
<i>a</i> [Å]	12.477(2)	10.578(2)	9.3818(18)	19.891(3)
<i>b</i> [Å]	17.529(3)	9.1589(19)	14.470(3)	8.2807(13)
<i>c</i> [Å]	19.792(3)	15.943(3)	28.554(5)	32.847(5)
α [°]	64.145(2)	90.00	88.542(3)	90.00
β [°]	78.987(2)	90.795(3)	85.980(2)	101.332(2)
γ [°]	89.269(2)	90.00	89.426(3)	90.00
<i>V</i> [Å ³]	3811.4(11)	1544.4(6)	3865.5(13)	5304.7(14)
<i>Z</i>	4	2	2	8
ρ_{calcd} , Mg m ⁻³	1.419	1.519	1.447	1.278
μ , mm ⁻¹	2.169	2.664	2.657	2.696
<i>F</i> (000)	1680	720	1732	2075
θ range for data collection [°]	2.193 - 26.763	2.30 - 25.45	1.41 - 25.14	2.22 - 25.39
no. of reflections collected	77094	15536	57729	30017
no. of independent reflections	14441	2840	13688	4837
Data / restraints / parameters	14441 / 0 / 937	2840 / 0 / 201	13688 / 1021 / 1215	4837 / 610 / 330
GooF	1.073	1.030	1.047	1.081
<i>R</i> 1, <i>wR</i> 2[<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0355, 0.0953	0.0423, 0.1113	0.0731; 0.1843	0.0537, 0.1287
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0452 / 0.0996	0.0503, 0.1162	0.0899; 0.1937	0.0701, 0.1355
largest diff peak, hole [e Å ⁻³]	0.697 / -0.766	1.833 / -0.538	3.952 / -0.784	1.634 / -0.718

^a*R*1 = $\Sigma||F_o| - |F_c|| / \Sigma|F_o|$; ^b*wR*2 = $[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{0.5}$