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Organolithium Compounds

Consecutive Donor-Base Exchange in Anthracenyllithium Compounds**

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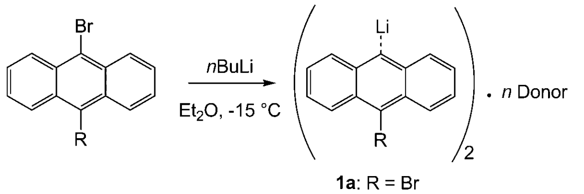
Dedicated to Professor Herbert W. Roesky on the occasion of his 75th birthday

Organolithium compounds are of outstanding importance as starting materials for numerous products in synthetic chemistry[1] and also in industrial processes.[2] Their remarkably wide range of applications spans from deprotonation of weakly acidic compounds to transfer reactions of organic groups or even anionic polymerization reactions. Since Schlenk and Holtz reported the first syntheses of organolithium compounds,[3] and the first crystal structure of a compound from this class (tetrameric ethyllithium) was successfully determined by Dietrich in 1963,[4] a large number of alkyl and aryl lithium reagents has been structurally characterized.[5] In hydrocarbon solvents, organolithium reagents form oligomers and their size significantly influences the reactivity. For the two compounds most commonly used in synthesis, *n*BuLi and *t*BuLi, the degree of oligomerization in solution was identified early on by cryoscopical and spectroscopical measurements. It was found that *n*BuLi[6] forms a hexamer whereas *t*BuLi[7] forms a tetramer in non-donating solvents. By addition of ethers, such as diethyl ether or THF, and especially by addition of tertiary amine donor bases, such as TMEDA or PMDETA, these oligomers can be disaggregated to smaller fragments, resulting in an enhanced reactivity.[8] This is illustrated by the benzylic deprotonation of toluene employing *n*BuLi, which is only feasible upon the addition of TMEDA.[9] In practice, mixtures of different donor bases are frequently used; however, the exact percentage of the single donor bases to give the most suitable complex is usually determined empirically, and the exact constitution of the reactive complex is unknown. It is most commonly presumed that the entire coordination sphere of the lithium atom is occupied by the strongest donor molecules available. Structural evidence for complexes in which organolithium compounds are coordinated by two different donor bases simultaneously are rare and their reproducibility is difficult.[10]

Using sterically demanding organolithium compounds, we embarked on monitoring the selective and consecutive donor base exchange. Herein, the complexes $[R(C_{14}H_8)Li\cdot\{Et_2O\}_n\cdot\{THF\}_m]_2$ were isolated and structurally characterized, and the lengths of the Li–C bonds of **1a** ($n=1$, $m=0$, R = Br), **2b** ($n=1$, $m=1/2$, R = Me), **3a** ($n=1$, $m=1$, R = Br), **4c** ($n=1/2$, $m=3/2$, R = Cl), and **5a** ($n=0$, $m=2$, R = Br) are monitored, because they provide information on the polarity of the bonds and thus shed some light on the expected reactivities of the formed complexes.

The degree of oligomerization, which mainly depends on the donor-base capacity, is additionally influenced by the steric demand of the alkyl or aryl carbanion, and is decreased with increasing size; for example, *n*BuLi is a hexamer whereas *t*BuLi forms a tetramer. By coordination of multidentate donor bases, the size of these aggregates can further be decreased, even to monomers: for example, $[PhLi\cdot Et_2O]_4$[11] > $[PhLi\cdot TMEDA]_2$[12] > $[PhLi\cdot PMDETA]$.[13] Upon combination of weak monodentate donor bases such as diethyl ether with organolithium compounds of substantial steric bulk, small, mostly dimeric aggregates are formed. In these dimers, the lithium atoms are sterically shielded in a way that the coordination sphere can not be filled entirely to the preferred coordination number of four.[14] Systems such as these are particularly suitable for monitoring the process of donor base uptake and exchange.

In the following investigation we selected anthracene, which can formally be described as a di*ortho*-substituted benzene. It is suitable as a proof-of-concept to facilitate the comparison to di*ortho*-substituted phenyllithium derivatives omnipresent in the literature. The brominated anthracene derivatives can easily be obtained by the reaction of the monosubstituted anthracenes with elemental bromine in solution.[15] Reacting *n*BuLi with bromoanthracenes gives the lithiated species in almost quantative yields (Scheme 1).[16]



1a: R = Br
1b: R = Me
1c: R = Cl

Scheme 1. Lithiation of substituted anthracene derivates from the corresponding bromides to give dimeric complexes.

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The aryl lithium compounds obtained by this reaction path exclusively form dimers when mono- or bidentate donors are added. If the lithiation is performed at $-15\,^{\circ}\mathrm{C}$ in diethyl ether, complexes of the composition $[\mathrm{R(C_{14}H_8)Li{\cdot}Et_2O}]_2$ (**1**) are obtained. Elemental analyses and NMR experiments show that the lithium atoms in these complexes have the relatively rare coordination number of three. Along with the steric demand of the anthracene carbanion, the bulk of the ether molecule is responsible for this coordination. The crystal structure analyses of these complexes confirm this result and show the rather unusual orientation of the carbanion in the dimer (Figure 1).[17]

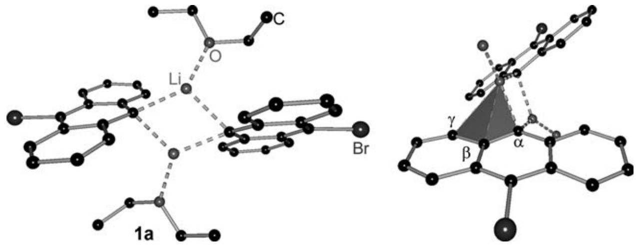
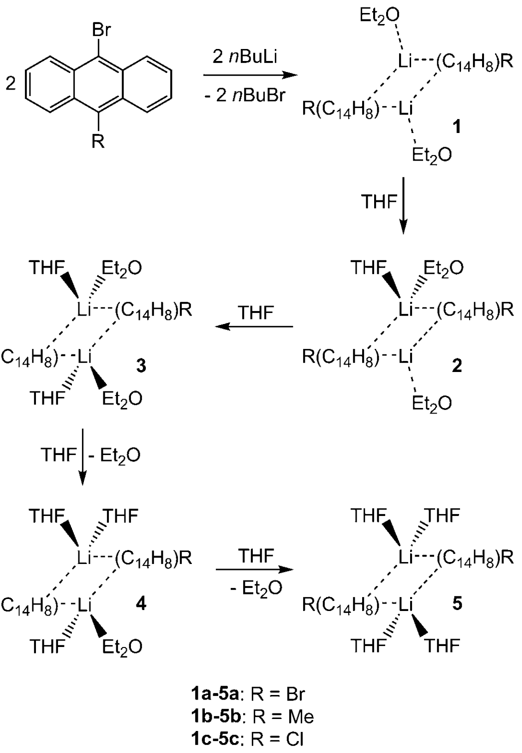


Figure 1. Crystal structure of **1a** (left; hydrogen atoms omitted), and a view of the allylic η^3-coordination of Li1 (right; carbon atoms of ether molecules and hydrogen atoms omitted for clarity). Only one of the two independent molecules in the asymmetric unit is shown. Selected bond lengths [Å]: Li1–C_α 2.211(4), Li1–C_β 2.720(4), Li1–C_γ 2.766(5), Li2–C_α 2.187(4), average Li–C_α 2.202, average Li–O 1.910.



Scheme 2. Mechanism of the consecutive substitution of Et_2O by THF in the complexes **1** to **5**.

All of the diethyl ether complexes of anthracenyl lithium that have been analyzed to date crystallize in the triclinic space group $P\bar{1}$. **1a** contains two dimers in the asymmetric unit. Unexpectedly, the anthracene planes are not oriented coplanar, but are tilted with an angle of 56.5(2)° relative to each other. Consequently, the central four-membered Li_2C_2 ring is not arranged orthogonal to the planes of the carbanions (60.50(15)° and 83.47(13)°). This orientation causes the lithium atom to move from the expected orthogonal position at the bisection of the central C_6 perimeter to an allylic bonding. In this coordination site it is formally η^3-coordinated (Figure 1, right), as is observed for example in benzyl-[18] or picolyllithium.[1f] The distance of the lithium atom to the C_γ atom is 2.211(4) Å, whereas that to the C_β atom is only 0.51 Å longer, and that is extended by another 0.05 Å. The coordination sphere of the η^3-bonded lithium atom is completed by one diethyl ether molecule.

Addition of exactly one equivalent of the stronger donor base THF does not initiate the expected exchange of donors, where one or both diethyl ether molecules might be replaced. THF removes the lithium atom from the η^3-coordination site and donates instead, because it has a much higher dipole moment (1.75 D for THF and 1.15 D for Et_2O)[19] and less steric demand (Scheme 2). The resulting compound $[\mathrm{(thf)(Et_2O)_2Li_2(C_{14}H_8R)_2}]$ (**2**) contains one threefold- and one fourfold-coordinated lithium atom. By addition of just one more equivalent of THF, the coordination sphere of the second lithium atom is extended to the coordination number four in $[\mathrm{(thf)_2(Et_2O)_2Li_2(C_{14}H_8R)_2}]$ (**3**). Further addition of a second THF molecule to the complex takes place selectively in the *trans* position relative to the first THF molecule. Unfortunately, this result cannot be rationalized by the energy difference between *cis* and *trans* geometries because the *cis* conformer is energetically favored and the difference is only $1.4\,\mathrm{kcal\,mol^{-1}}$ (DFT gas phase optimizations at the B3LYP/6-311G* level of theory).[20]

The exchange of donor molecules is not observed until a third equivalent of THF is added. The weaker donor base Et_2O is replaced by the stronger donor THF to form the complex $[\mathrm{(thf)_3(Et_2O)Li_2(C_{14}H_8R)_2}]$ (**4**). From four or more equivalents of THF, the ligand exchange is complete, giving $[\mathrm{(thf)_4Li_2(C_{14}H_8R)_2}]$ (**5**). After the second equivalent of THF is added, both lithium atoms adapt the predominant coordination number of four and π-electron density is not longer required to complete their coordination sphere. This allows the anthracene planes to relax to their anticipated co-parallel orientation (Figure 2). The Li–C bond lengths in the various complexes are indicative of the reactivity, because it is likely that their polarity decreases with increasing length and that it is gradually easier to cleave a longer bond in polar solvents. As anticipated, they increase from **1** to **5**, because the better donor base THF supplies more electron density to the lithium atoms and the lithium—carbanion interaction is increasingly less required. The same trends were detected in many parent basic organolithium compounds for various electron-releasing carbanions.[14a] However, the bond lengths unexpectedly reach a maximum in the hetero-donated complex **3** with only two THF molecules, and not in complex **5**, which is

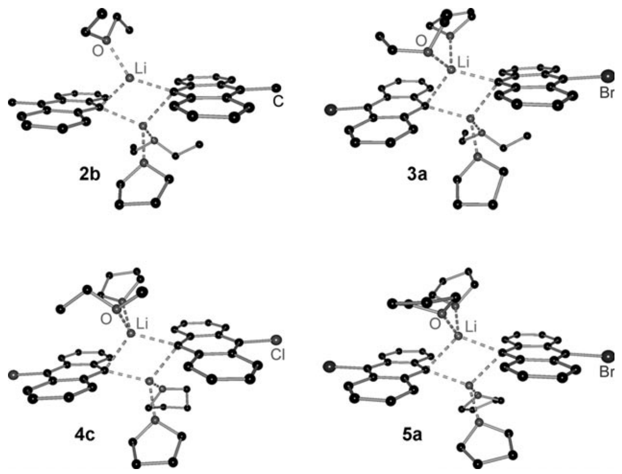


Figure 2. Crystal structures of the complexes **2b**, **3a**, **4c**, and **5a** (hydrogen atoms not depicted). Selected bond lengths [Å]: average Li–C_α 2.276 (**2b**), 2.3183 (**3a**), 2.307 (**4c**), 2.299 (**5a**), average Li–O 1.992 (**2b**), 2.035 (**3a**), 2.036 (**4c**), 1.985 (**5a**).

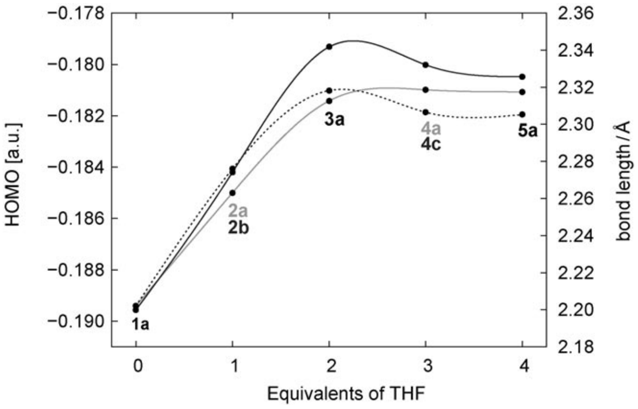


Figure 3. Correlation between HOMO energies as a measure of reactivity and averaged Li–C_α bond lengths in compounds **1**–**5**. For the HOMO energies, only compounds with R = Br were used. Dark gray line: Theoretical bond lengths for **1a**, **2b**, **3a**, **4c**, **5a**; dotted line: experimental bond lengths for **1a**, **2b**, **3a**, **4c**, **5a**; light gray line: HOMO energies for **1a**, **2a**, **3a**, **4a**, **5a**.

exclusively coordinated by four molecules of the stronger donor base THF (see also the Supporting Information). This illustrates well the interplay of donor capacity and steric requirements. The most electron density supplied by the stronger donor base would not necessarily give the most reactive complex with the longest Li–C bond.

To test the hypothesis of rising reactivity with an increasing amount of THF, accompanied by elongating Li–C_α bond lengths, we performed gas-phase geometry optimizations with subsequent frequency calculations of **1** to **5** at the B3LYP/6-311G* level of theory.[20] These theoretical values were then compared to the experimental bond lengths. The latter are well reproduced, with a tendency to elongate long bonds (see Supporting Information).[21] The addition of the first two equivalents of THF obviously has a distinct effect on the average bond distances, whereas the third and fourth equivalent do not affect the distances much.

A well-known measure of molecular reactivity is suggested by the orbital energies of the HOMOs (towards electrophilic attacks) and LUMOs (nucleophilic attacks).[22] Their absolute values may depend on the total number of electrons in the molecule, as these determine the number of molecular orbitals. Therefore it is advisable to compare only molecules with the same residue R. As this class of substances acts as nucleophiles, their reactivity with respect to electrophilic attacks is important, which is given by the HOMO energies.[22] The higher the HOMO energy, the easier an electron is donated into an acceptor orbital.

Figure 3 shows the increase of the HOMO energies with increasing equivalents of THF and with increasing average bond lengths for R = Br. Similar curves on different absolute values are obtained for R = Me and R = Cl. It should be noted that two scales are used in Figure 3. Whilst the bond lengths from theory and experiment show a maximum at **3** (two THF and two Et_2O), the HOMO energies reach a plateau at **3**. Thus the hypothesis of increasing molecular reactivity with increasing average Li–C_α bond lengths is supported by gas-phase calculations when the residue is the same. The kinetic effect of the two THF and two bulkier Et_2O donor molecules is not reflected by the calculations.

In conclusion, the selective and consecutive donor-base addition and exchange in the same lithiumaryl carbanion complex was monitored by structural determination. Unequivocally, it is feasible by stoichiometric addition of a second donor base to fine-tune the composition of a mixed-base complex. The Li–C bond lengths and hence the reactivity do not linearly scale to an increasing amount of the better donor base in the complex. The required amounts of donor bases to enhance the reactivity can be adjusted far more accurately than previously anticipated. Thus, the formation of hetero-donor base complexes should be taken into account when tailoring the reactivity of an organolithium compound. Especially in reactions where multiple functional groups are present, the mixed-base fine-tuning of the reactivity might be the crucial step to adapt the reactivity to enhanced regio- and enantioselectivity.

Experimental Section

1: A suspension of the particular bromoanthracene (10 mmol) in diethyl ether (80 mL) was cooled to −15 °C and exactly 10 mmol of a 2.25 M *n*BuLi solution in hexane was added dropwise over 30 min. The clear orange solution thus obtained was stirred for 30 min at 0 °C and then the amount of solvent was decreased to one third of the original volume in vacuo. Subsequently, the solution was cooled to −78 °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. To give crystals, complex **1** (ca. 0.5 g) was dissolved in cold diethyl ether (10 mL). An insoluble residue was separated from the solution by filtration and the solution was then stored at −25 °C. After 24 h, crystals of $[\{LiAnR\cdot Et_2O\}_2]$ (**1**) that were suitable for diffraction experiments were obtained.

Crystallization of $[\{LiAnR\cdot donor\}_2]$ (**2**–**5**): Complex **1** (0.1 mmol) was dissolved in diethyl ether (10 mL) and cooled to −15 °C. The particular equivalents of cold THF were added slowly, and an insoluble residue was thereafter removed by filtration. The solution was stored at −25 °C for crystallization and after ca. 24 h crystals suitable for diffraction experiments were obtained.

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[17] Crystallographic details: Shock-cooled crystals were selected and mounted under nitrogen atmosphere using the X-TEMP2 [T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615] on a Bruker SMART-APEXII Quazar diffractometer with D8 goniometer (100 K, $\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å; INCOATEC Quazar mirror optics), for **2b** and **5a** data were collected on a Bruker APEXII Ultra diffractometer with D8 goniometer (100 K $\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å; INCOATEC Helios mirror optics). The structures were solved by direct methods (SHELXS) and refined on F^2 using the full-matrix least-squares methods of SHELXL [G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112]. CCDC 775594 (**1a**), CCDC 775595 (**2b**), CCDC 775596 (**3a**), CCDC 775597 (**4c**), and CCDC 766244 (**5a**) contain 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. Space group, cell parameters and R values with $[I > 2\sigma(I)]$: **1a**: $P\bar{1}$, $a = 14.9782(12)$, $b = 15.2917(12)$, $c = 15.4914(12)$ Å, $\alpha = 63.9660(10)$, $\beta = 87.2590(10)$, $\gamma = 82.3670(10)^\circ$, $wR2 = 0.0802$, $R1 = 0.0308$; **2b**: $P\bar{1}$, $a = 8.369(2)$, $b = 15.2917(12)$, $c = 17.613(5)$ Å, $\alpha = 99.325(3)$, $\beta = 101.564(3)$, $\gamma = 94.111(3)^\circ$, $wR2 = 0.1056$, $R1 = 0.0419$; **3a**: $P\bar{1}$, $a = 12.3301(18)$, $b = 12.3701(19)$, $c = 14.456(2)$ Å, $\alpha = 82.039(3)$, $\beta = 66.565(3)$, $\gamma = 75.547(2)^\circ$, $wR2 = 0.0961$, $R1 = 0.0411$; **4c**: $P\bar{1}$, $a = 12.269(2)$, $b = 12.412(2)$, $c = 14.318(3)$ Å, $\alpha = 81.590(3)$, $\beta = 67.146(3)$, $\gamma = 73.993(3)^\circ$, $wR2 = 0.1557$, $R1 = 0.0618$; **5a**: $P\bar{1}$, $a = 12.477(2)$, $b = 17.529(3)$, $c = 19.792(3)$ Å, $\alpha = 64.145(2)$, $\beta = 78.978(2)$, $\gamma = 89.269(2)^\circ$, $wR2 = 0.0992$, $R1 = 0.0451$. Further details regarding the structure determinations can be found in the Supporting Information.

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