Crystal Structures of [PhLi·(−)-sparteine]₂, [PhOLi·(−)-sparteine]₂, and the Mixed Aggregate [PhLi·PhOLi·2(−)-sparteine]

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Summary: Crystal structure determination of adducts of (−)-sparteine and PhLi, (−)-sparteine and PhOLi and of (−)-sparteine and PhLi/PhOLi reveal a four-membered ring with two lithium centers, each capped by a (−)-sparteine ligand, as central motif of all structure. Quantum-chemical calculations show that the mixed aggregate [PhLi·PhOLi·2(−)-sparteine] is energetically more favorable than the model system {¹/₂[PhLi·(−)-sparteine]₂ + ¹/₂[PhOLi·(−)-sparteine]₂}.

Although altering the reactivity of organolithium reagents by using donor solvents or chelating ligands is of significant importance in optimizing their preparative use, the origin of these mostly empirical results is not well understood.[1] Crystal structures of coordinated organolithium reagents can provide additional insight into the stereo-, regio-, and chemoselectivity of these compounds.

Depending on the coordinating ligand, X-ray crystallographic studies of PhLi reveal tetrameric,[2a] trimeric,[2a] dimeric,[2b] or monomeric[2c] structures. In the case of (−)-sparteine-coordinated simple organolithiums, the crystal structures of *t*-BuLi,[3a] *n*-BuLi and *i*-PrLi,[3b] and MeLi and PhLi[3c,d] adducts were determined. C_2-symmetric dimers were found for [MeLi·(−)-sparteine]₂ (**1**) (Figure 1) and [*n*-BuLi·(−)-sparteine]₂. In the case of PhLi, excess PhLi and (−)-sparteine forms the 4:2 aggregate [(PhLi)₄·{(−)-sparteine}₂] (**2**)[3d] (Figure 1).

Since the exceptional reactivity patterns of mixed aggregates are gaining more interest[5] and, in comparison to sp³ alkyllithium reagents, only little is known about sp² organolithium compounds and their aggregation,[6] we decided to investigate the solid-state structures of adducts between (−)-sparteine and PhLi (**3**), PhOLi (**5**), and the mixed aggregate **4** (Chart 1).

Since the PhLi/TMEDA[2b] aggregate forms a dimer, the analogous combination PhLi/(−)-sparteine would seem to be sterically overcrowded. We would thence expect comparatively small changes in the lithiated species to have a significant

structural effect, perhaps even leading to a mixed aggregate. PhOLi is less bulky than PhLi; therefore, we decided to study the mixtures PhLi/(−)-sparteine, PhOLi/(−)-sparteine, and PhLi/PhOLi/(−)-sparteine.

When PhLi and (−)-sparteine were mixed in a 1:1 ratio in pentane/diethyl ether, two different aggregates were obtained. The 4:2 aggregate **2** was found in larger blocks, while [PhLi·(−)-sparteine]₂ (**3**) was obtained, in lower quantities, as smaller rhombic crystals (Figure 2);[7a] these were identified as possessing the orthorhombic space group $C222_1$. The asymmetric unit contains one adduct of PhLi·(−)-sparteine, the whole dimer being formed by a C_2 symmetry operation. The arrangement in the dimer appears overcrowded, explaining the preference for the less sterically strained 4:2 aggregate **2**.

The mixed aggregate [PhLi·PhOLi·2(−)-sparteine] (**4**) crystallizes in the monoclinic crystal system, space group $P2_1$, and was prepared by mixing PhLi, PhOLi, and (−)-sparteine (ratio 1:1:2) in pentane/diethyl ether (Figure 3).[7b]

As expected, steric crowding in the PhLi/(−)-sparteine part is decreased compared to **3**. The dimer [PhOLi·(−)-sparteine]₂

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(7) (a) Crystal data for **3**·*n*-pentane: C₄₂H₆₂Li₂N₄·*n*-C₅H₁₂, M_r = 708.98, orthorhombic, a = 14.581(3) Å, b = 22.782(5) Å, c = 12.847(3) Å, V = 4267.6(15) Å³, $C222_1$ (No. 20), Z = 4, μ = 0.063 mm⁻¹, 10 801 reflections measured with 2θ in the range 3.64−50.00°, 3751 unique reflections, R1 = 0.0532 ($I > 2\sigma(I)$), wR2(F_o^2) = 0.1179 (all data). (b) Crystal data for **4**·*n*-pentane: C₄₂H₆₂Li₂N₄O·*n*-C₅H₁₂, M_r = 724.98, monoclinic, a = 9.694-(2) Å, b = 16.621(3) Å, c = 13.931(3) Å, β = 104.16(3)°, V = 2176.3(7) Å³, $P2_1$ (No. 4), Z = 2, μ = 0.065 mm⁻¹, 28 587 reflections measured with 2θ in the range 5.00−50.00°, 7678 unique reflections, R1 = 0.0556 ($I > 2\sigma(I)$), wR2(F_o^2) = 0.1477 (all data). (c) Crystal data for **5**·*n*-pentane: C₄₂H₆₂Li₂N₄O₂·*n*-C₅H₁₂, M_r = 740.98, monoclinic, a = 9.7174(18) Å, b = 16.668(3) Å, c = 14.420(2) Å, β = 106.20(2)°, V = 2242.9(7) Å³, $P2_1$ (No. 4), Z = 2, μ = 0.066 mm⁻¹, 20 251 reflections with 2θ in the range 3.26−50.00°, 7899 unique reflections, R1 = 0.0606 ($I > 2\sigma(I)$), wR2(F_o^2) = 0.1486 (all data). The solvent molecule in **5**·*n*-pentane is disordered and has been refined using a disorder model. For **3**−**5**, the refinement of the correct stereoisomer is unambiguous, due to the known and fixed configurations at the (−)-sparteine ligand (Flack parameters not significant). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 271615 (**3**), CCDC 271616 (**4**), and CCDC 271617 (**5**).

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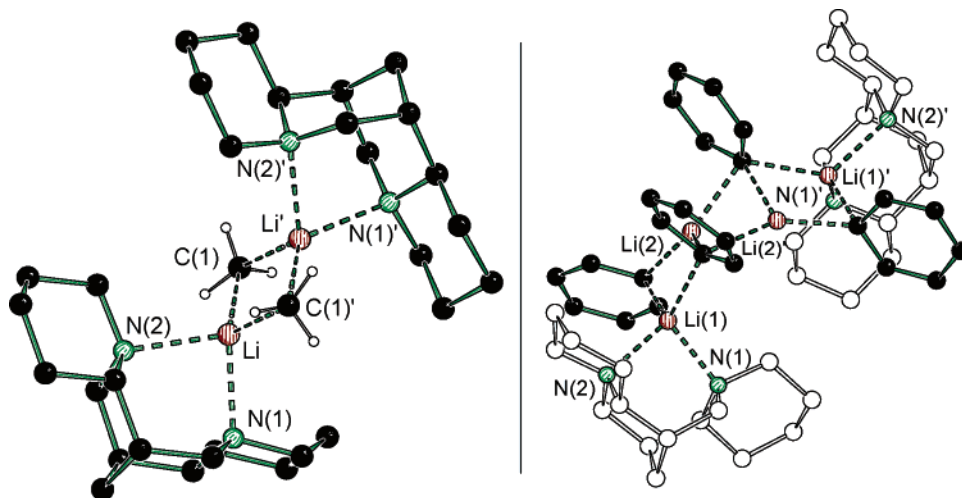
Figure 1. Crystal structures of [MeLi·(−)-sparteine]$_2$ (**1**) (left) and [(PhLi)$_4$·{(−)-sparteine}$_2$] (**2**) (right) (*Schakal* plots[4]).[3c,d]

Chart 1

3   **4**   **5**
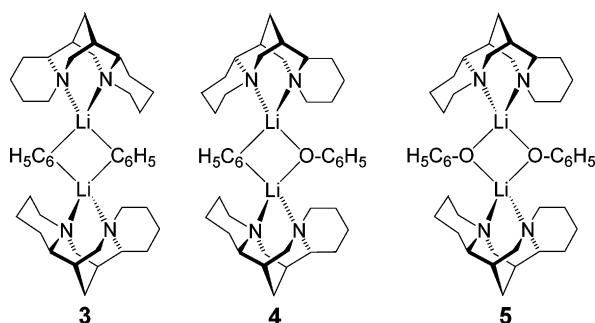
(**5**) crystallized from a 1:1 mixture of PhOLi and (−)-sparteine in pentane/diethyl ether in the space group $P2_1$ (Figure 4).[7c]

The dominant structural principles for alkoxides are the ladder, the ring-ladder, and the stacked-ring architecture. Mixed aggregates with alkyllithiums can often be described as tetramers and hexamers where alkoxy groups have been exchanged for alkanide units.[8] This work presents the first example of a mixed aggregate between an aryllithium and a lithium aryloxide with the hitherto unknown structural motif of a single C−Li−O−Li ring for a mixed CLi/OLi aggregate.[6]

The central element of all three crystal structures presented here is a single four-membered ring containing two metalated
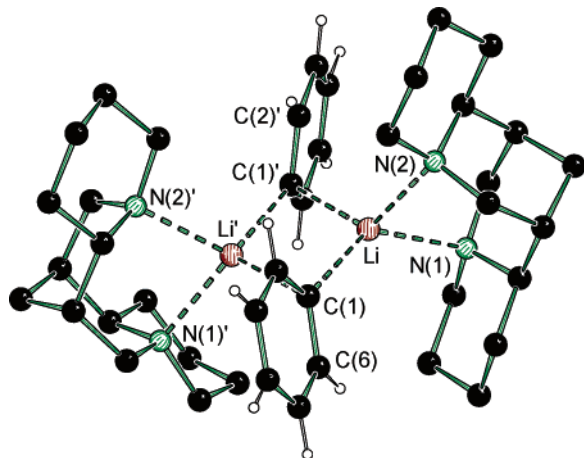
Figure 2. Molecular structures of [PhLi·(−)-sparteine]$_2$ (**3**) in the solid state (*Schakal* plot[4]). Selected bond lengths (Å) and angles (deg) of **3**: C(1)−Li = 2.250(5), C(1)−Li′ = 2.347(5), Li−N(2) = 2.212(5), Li−N(1) = 2.255(5); Li−C(1)−Li′ = 73.82(18), N(2)−Li−N(1) = 81.62(16), C(1)−Li−C(1)′ = 106.13(18).
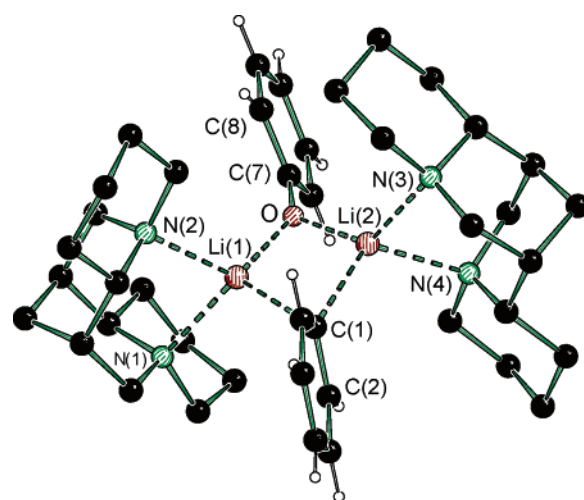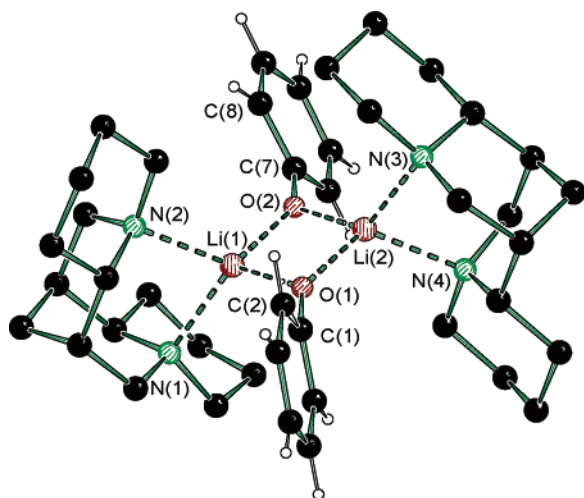

Figure 3. Molecular structures of [PhLi·PhOLi·2 (−)-sparteine] (**4**) in the solid state (*Schakal* plot[4]). Selected bond lengths (Å) and angles (deg) of **4**: C(1)−Li(1) = 2.276(5), C(1)−Li(2) = 2.280(5), C(7)−O = 1.281(3), Li(1)−O = 1.895(5), Li(1)−N(2) = 2.173(5), Li(1)−N(1) = 2.216(5), Li(2)−O = 1.918(5), Li(2)−N(4) = 2.186(5), Li(2)−N(3) = 2.196(5); Li(1)−C(1)−Li(2) = 70.13(17), Li(1)−O−Li(2) = 86.69(19), O−Li(2)−C(1) = 101.0-(2), O−Li(1)−C(1) = 101.9(2), N(2)−Li(1)−N(1) = 83.63(18), N(4)−Li(2)−N(3) = 82.77(17).

centers and two lithiums, the latter capped by two diamine ligands. In the crystal structures of **3** and **5**, only one of the two possible stereoisomers is observed. **3** contains a C_2 axis in the center of the four-membered ring, while **5** shows the other possible stereoisomers with a formal C_2 axis which bisects the four-membered ring along the two phenolate units. Three stereoisomers are possible for the mixed aggregate **4**, but only one is in evidence here. In **4** and **5**, the relative orientations of the (−)-sparteine ligands are identical.

In the C_2 dimeric structure [PhLi·TMEDA]$_2$,[2b] the following significant bond lengths (Å) and angles (deg) were determined: Li−C(1) = 2.208(6), Li−C(1′) = 2.278(6), Li−N(1) = 2.177(4), Li−N(2) = 2.208(4); C(1)−Li−C(1′) = 105.6(2), Li−C(1)−Li′ = 67.4(1). In comparison to this less crowded dimeric structure, the Li−C bond distances of **3** are elongated by 0.05 and 0.07 Å, respectively. Furthermore, Li−C(1) (2.250-(5) Å) is about 0.10 Å shorter than Li′−C(1) (2.347(5) Å),

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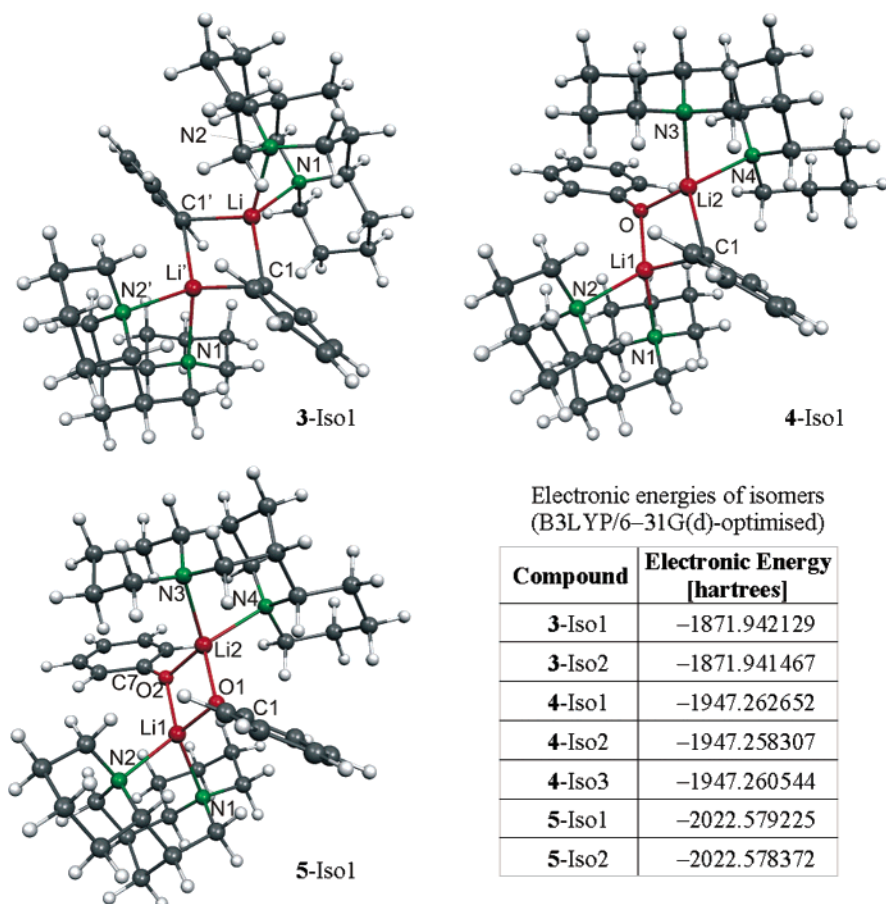
Figure 4. Molecular structure of [PhOLi·(−)-sparteine]₂ (**5**) in the solid state (*Schakal* plot[4]). Selected bond lengths (Å) and angles (deg): Li(1)−O(2) = 1.899(7), Li(1)−O(1) = 1.911(6), Li(1)−N(2) = 2.106(8), Li(1)−N(1) = 2.171(8), Li(2)−O(1) = 1.868(6), Li(2)−O(2) = 1.952(6), Li(2)−N(4) = 2.111(7), Li(2)−N(3) = 2.129(7), Li(2)−O(1)−Li(1) = 88.1(3), Li(1)−O(2)−Li(2) = 86.0-(2), N(2)−Li(1)−N(1) = 85.0(3), N(4)−Li(2)−N(3) = 85.8(2), O(2)−Li(1)−O(1) = 93.1(3), O(1)−Li(2)−O(2) = 92.8(3).

leading to a more distorted four-membered ring. The Li−N distances are about 0.04 Å longer in **3**, and the Li−C−Li′ angle in **3** is 6° wider than in the TMEDA structure. All these parameters can be explained by the steric repulsion of the two (−)-sparteine ligands and the phenyl groups opposite to each other, which leads to a widening of the four-membered ring in

3 with respect to the TMEDA dimer. The mixed aggregate [PhLi·PhOLi·2(−)-sparteine] (**4**) is sterically less encumbered than [PhLi·(−)-sparteine]₂ (**3**). Replacement of a phenyl with a phenoxy group results in bond lengths and distances comparable to those in the TMEDA dimer. The bond lengths Li(1)−C(1) (2.276(5) Å) and Li(2)−C(1) (2.280(5) Å) are identical within the error margin. The Li(1)−C(1)−Li(2) angle in **4** (70.13(17)°) is compressed about 3° compared to that in **3** but is still 3° wider than in [PhLi·TMEDA]₂. In striking contrast to [PhLi·(−)-sparteine]₂ (**3**), the Li−N bond lengths in **4** and the TMEDA dimer are virtually identical. The phenolate dimer [PhOLi·(−)-sparteine]₂ (**5**) (Figure 4) shows the less distorted four-membered ring. The Li−O bond lengths of **5** are identical with those of **4**, as are the Li−O−Li angles. However, the Li−N bond distances differ by about 0.07 Å (longest, Li(1)−N(1) = 2.171(8) Å; shortest, Li(1)−N(2) = 2.106(8) Å). They are significantly shorter than the Li−N bond distances in [PhLi·TMEDA]₂ and slightly shorter even than in [MeLi·(−)-sparteine]₂ (**1**) but are identical within the margin of error in comparison to the bond length in [(PhLi)₄·{(−)-sparteine}₂] (**2**). This indicates that (−)-sparteine is a stronger ligand than TMEDA for such systems.

Reich and co-workers have shown that, for different aggregate states of PhLi, certain reactions proceed at different rates and even yield different products.[1c] Mixed aggregates such as **4** have to be considered, for example, in reactions of PhLi with ketones, where alkoxides are formed as products. The question arises whether the mixed aggregate **4** is thermodynamically favored over the pure dimers **3** and **5**, as indicated by the isolation of **4** in the crystal. By quantum-chemical analyses the structures of all possible stereoisomers (**3**-Iso1-2, **4**-Iso1-3, **5**-Iso1-2) were

Electronic energies of isomers (B3LYP/6−31G(d)-optimised)

Compound	Electronic Energy [hartrees]
3-Iso1	−1871.942129
3-Iso2	−1871.941467
4-Iso1	−1947.262652
4-Iso2	−1947.258307
4-Iso3	−1947.260544
5-Iso1	−2022.579225
5-Iso2	−2022.578372

Figure 5. *Molekel* plots[11] of optimized [PhLi·(−)-sparteine]₂ (**3**-Iso1), [PhLi·PhOLi·2(−)-sparteine] (**4**-Iso1) and [PhOLi·(−)-sparteine]₂ (**5**-Iso1) (B3LYP/6-31G(d)).

energy optimized at the B3LYP/6-31G(d) level[9,10] of theory. The calculated structures with the lowest energies in the gas phase are the isomers found in the solid state by X-ray structure analysis. We were able to show that the model system [PhLi·PhOLi·2 (−)-sparteine] is energetically more favorable than the model system {$^1/_2$[PhLi·(−)-sparteine]$_2$ + $^1/_2$[PhOLi·(−)-sparteine]$_2$} by 5.2 kJ/mol (Figure 5). This underscores the trend for the formation of the mixed aggregate **4** in the experiment.

The structural motif of mixed aggregates, which has been found in alkyllithium/alkoxylithium systems,[5] has now been determined for the first time for an aryllithium/aryloxylithium system. The exchange of one anionic ligand by another (Ph/PhO) does not change the central motif in the structures of **3**−**5**. This principle has already been described in the literature[12] for tetramers and hexamers (with one exception[5d]). The four-membered ring is the smallest aggregate possible. Such four-membered rings, containing two metalated centers and two lithiums, are known for mixed aggregates, but to the best of

our knowledge, this is the first structurally characterized example of a mixed aggregate with aryloxide that has only a four-membered ring as the central structural feature.

The results of the crystal structures, in combination with the quantum-chemical analysis, indicate that the mixed aggregate **4** is thermodynamically favored over the dimers **3** and **5**. Since **3** seems to be sterically encumbered, it releases some pressure by forming [(PhLi)$_4$·{(−)-sparteine}$_2$] (**2**), unless phenyl is substituted by some other group (e.g. phenoxy). Therefore, a new aggregate is formed and it can be expected that other anionic additives or reaction products also have a significant influence on aggregation and reactivity of the system PhLi/(−)-sparteine. Some interesting points should be noted. The (−)-sparteine ligands in **4** and **5** have a different relative orientation to each other than in [PhLi·(−)-sparteine]$_2$ (**3**). Mixing PhLi, PhOLi, and (−)-sparteine in a 1:1:2 ratio gives a defined reagent, and only one isomer of the mixed compound [PhLi·PhOLi·2(−)-sparteine] (**4**) is observed in the solid state. In combination with NMR studies in solution, which are currently in progress, it has to be determined if the defined mixed aggregate formation of [PhLi·PhOLi·2(−)-sparteine] (**4**) with a new (−)-sparteine orientation in dimers does have an impact on either reactivity or selectivity in comparison to [PhLi·(−)-sparteine]$_2$ (**3**).

Supporting Information Available: Experimental, computational, and crystallographic data (including ORTEP plots and CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

OM050794W

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(10) Computational methods: All calculations were carried out on gas-phase structures. Structure optimizations at the B3LYP/3-21G and B3LYP/6-31G(d) levels were performed using Gaussian 98. The basis for the starting structures were the coordinates of the X-ray structural analyses and corresponding stereoisomers. Two stereoisomers have to be considered for the compounds **3** and **5**. The four stereoisomers of **4** that can be arranged are reduced to three, since two can be transformed into each other. Energy minimization and calculation at the B3LYP/3-21G level gave the same conformers as calculations at the B3LYP/6-31G(d) level. All the frequency calculations were carried out at the B3LYP/3-21G level because of size and showed no negative frequencies.

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