Insights into the Metalation of Benzene and Toluene by Schlosser's Base: A Superbasic Cluster Comprising PhK, PhLi, and *t*BuOLi**

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Abstract: The metalation of benzene by Schlosser's base (nBuLi/tBuOK) occurs smoothly in THF at low temperatures to afford a discrete mixed-metal Li_2K_4 cluster that contains phenyl anions and tert-butoxide. The aggregate itself exhibits superbasic behavior by metalating toluene. The delocalized benzyl anion obtained this way π bonds to potassium counterions, thereby creating a 2D coordination polymer.

Since its discovery and first-time investigation by Schlosser^[1] and Lochmann et al.,^[2] the combination of potassium *tert*butoxide and alkyllithium compounds has developed into a stock item for organometallic, organic, and synthetic chemists. As a consequence of the synergic metalation properties of the resultant superbasic "LICKOR" system, the deprotonation and subsequent functionalization of a wide range of substrates has been considerably facilitated.^[3] The powerful metalating properties of LICKOR bases have spawned a broad variety of exciting preparative and structural investigations in the field of multicomponent synergic deprotonating reagents.^[4]

The efficient metalation of the most fundamental arenes benzene and toluene by the LICKOR base is a clear illustration of the strong metalating power of this exceptional base mix.^[5] However, despite the synthetic potential of these and related metalation reactions, structural examples derived from reactions with the classic Schlosser's base mixture "*n*BuLi/*t*BuOK" remain comparatively scarce.^[6] The elucidation of species responsible for the superbasic behavior remains an important object of current research.^[7]

The practical handling of *n*BuLi/*t*BuOK in THF allows for homogeneous reactions with a high degree of chemoselectivity, while the mixture shows poor solubility in aliphatic solvents.^[2] Following our studies on the metalation of functionalized arenes with Schlosser's base^[8] and mixed Li/ K amides,^[9] our current investigations centered on the deprotonation of the unsubstituted aromatic systems benzene and toluene by the bimetallic superbase.

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Treatment of *n*BuLi/*t*BuOK in THF at -78 °C with an excess of benzene afforded an orange solution, even at low temperatures and short reaction times. Concentration of the solution at a maximum temperature of -40 °C and subsequent storage of the reaction mixture at -78 °C afforded a crop of orange crystals of compound **1**. The aggregate crystallizes from THF/benzene in the monoclinic crystal system in the space group *C*2/*c*. The asymmetric unit contains one half of the aggregate alongside one half-molecule of cocrystallized benzene. Thus, the aggregate exhibits *C*₂-symmetry along the C1-O1 axis (Figure 1).



Figure 1. Molecular structure of $[(PhK)_4(PhLi)(tBuOLi)(THF)_6(C_6H_6)_2]$ (1; hydrogen atoms omitted for clarity; only the shortest C-K contacts for each phenyl moiety are shown; symmetry operation: -x + 1, y, -z + 1/2). Selected bond lengths (Å) and angles (°): C1-K1' 3.485(4), C4-Li1' 2.274(8), C4-K1 2.867(5), C4-K2 3.030(4), C10-Li1 2.494(8), C10-K1 3.442(4), C10-K2 3.145(2), C11-K2' 3.353(5), C14-Li1 2.268(7), C14-K2 3.092(4), C15-K2' 3.229(4), K1-O1 2.731(2), K1-O2 2.625(6), K2-O4 2.729(3), K2-O3 2.722(4), Li1-O1 1.950(7); Li'-C4-K1 69.9(2), Li'-C4-K2 68.4(3), K1-C4-K2 114.2(2), Li'-C10-Li 73.3(3), Li-C10-K2 138.0(2), Li-C10-K2' 64.7(2).

We were delighted to find that the composition of **1** was $[(PhK)_4(PhLi)(tBuOLi)(THF)_6(C_6H_6)_2]$ and contained each of the superbase's components. Its central unit comprises a phenyllithium and lithium *tert*-butoxide moiety. The lithium atoms, the oxygen atom of the butoxide, and the carbanionic carbon center of the phenyl group form a four-membered ring with considerably elongated C-Li contacts of 2.494(8) Å.^[10] This central motif is surrounded by a twisted eight-membered ring formed with four phenylpotassium units. The four phenyl groups adopt a twisted conformation with respect to the Li₂

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edge, with two ipso-carbon atoms pointing towards each of the two lithium centers.^[11] The potassium centers are arranged between the four outer phenyl groups: two of them exhibit contacts to the oxygen atom of the alkoxide moiety [K1-O1 2.731(2) Å],^[12] while two exhibit contacts to the *ipso-* and ortho-carbon atoms of the inner phenyl group [C10-K2 3.145(2) Å, C11-K2 3.250 Å, C11-K2' 3.353(5) Å]. The former are coordinated by one THF molecule, while the latter potassium centers are each coordinated to two THF molecules and with another η^1 contact to an additional coordinating benzene molecule. Thus, the Li₂ unit serves as the core of the aggregate, with the "hard" anions-the butoxide anion and phenyl moieties-facing towards them. The potassium centers are arranged around this core, in an eight-membered ring arrangement. Their contacts to the phenyl groups are approximately perpendicular to those of the lithium centers. This signifies the softer potassium's preference for interaction with π electrons (from above or below the arene plane); this is in contrast to the smaller and harder lithium cation, which prefers an "in-plane" interaction with the localized carbanion. To the best of our knowledge, 1 constitutes the first example of a bimetallic aggregate containing all constitutents of the LICKOR base and a simple metalated hydrocarbon substrate. Thus, 1 bridges the knowledge gap between known "classical" organopotassium structures^[13] and related bimetallic aggregates derived from "alkali metal mediated metalations" or bimetallic "ate" complexes.^[14]

The substrate sensitivity of bimetallic K/Li metalations can be exemplified by the benzylic deprotonation of toluene by Schlosser's base under identical conditions. When an excess of toluene was added to *n*BuLi/*t*BuOK in THF at -78 °C, the solution immediately turned brightly orange, thus signifying the onset of lateral metalation in the benzylic position.^[15] Concentrating the reaction mixture and storage at -78 °C afforded orange crystalline needles of benzylpotassium solvate **2** (Figure 2).

Compound 2 crystallizes from THF/pentane in the orthorhombic crystal system in the space group Pbam. In contrast to mixed-metal 1, it has the formal composition $[(BnK)_3(THF)_4]_{\infty}$, with the fragment $[(BnK)_{1.5}(THF)_2]$ contained in the asymmetric unit. It forms a sheetlike 2D polymeric structure with a packing pattern which gives rise to two distinct benzyl anionic moieties and three different coordination environments of the potassium centers: The benzyl unit C8–C12 binds to two cations (K1 and K2) in a C_{v} symmetric environment (mirror plane K1-C8-C12-K2), with K1 being located "above" the arene plane and with a short contact to the benzylic center and a slightly longer contact to the ipso-carbon atom (C8-K1 3.068 Å; C9-K1 3.153 Å). K2 is located "below" the arene plane with a η^6 contact to the phenyl moiety, which is slightly shifted towards the paracarbon atom (C9-K2 3.288 Å, C12-K2 3.102 Å). The second benzylic unit C1-C7 displays contacts to three different potassium centers, with K1 and K2 on one and K3 on the other side: K1 exhibits η^3 coordination by an ortho-, ipso-, and benzylic carbon atom while K2 experiences a η^5 coordination through its ortho-, meta-, and para-carbon atoms (C5-K3 3.083 Å, C7-K3 3.485 Å). On the other side of the plane, K3 is



Figure 2. Molecular structure of $[(BnK)_3(THF)_4]_\infty$ (2; some hydrogen atoms are omitted for clarity). The gray carbon atoms are symmetry-equivalent positions, included to visualize the coordination environment of the potassium centers (symmetry operations: #1': *x*, *y*, −*z*+1; #2": *x*, *y*, −*z*+2; #3": *x*+1/2, −*y*+3/2, −*z*+2). Selected bond lengths (Å): C1-C2 1.367(5), C1-K1 3.014(4), C1-K3 3.515(5), C2-K3 2.965(3), C2-K1 3.294(3), C3-K3 3.048(3), C3-K2 3.485(3), C4-K2 3.205(3), C7-K1 3.383(4), C7-K2 3.469(3), C8-K1' 3.068(5), C8-C9 1.367(7), C9-K1' 3.153(4), C9-K2 3.288(4), K2-C6" 3.191(3), K2-C4" 3.205(3), K2-C10" 3.221(3), K3-C1 2.629(4), K3-O2 2.696(4), K3-C2" 2.965(3), K3-C3" 3.048(3), K3-C7" 3.185(3), K3-C4"'' 3.270(3), K3-C6"'' 3.400(3).

 η^6 coordinated by all six phenyl carbon atoms, with a sight slant towards the ipso-carbon atom (C2-K3 2.965 Å, C5-K3 3.441 Å).^[9] A THF solvent molecule bridges between K1 and K2, and an additional THF coordinates exclusively to K1. K3 is coordinated by two further THF donors. The arrangement of three potassium centers around the benzylic unit C1-C7 results in a distortion of its planar geometry: the benzylic carbon atom C1 is bent significantly out of the arene plane C2-C7 by 0.143 Å.^[16] Quantum-chemical model calculations support this deformation of a benzyl anion which is asymmetrically embedded between three potassium centers. Despite this deformation, the C–C bond lengths are in the range of those found in the second unit C8-C12 or in related monomeric benzylpotassium structures.^[17] At only 1.367 Å, the length of the bonds between the benzylic and ipso-carbon atoms (C1-C2 and C8-C9) are among the shortest recorded for benzylmetal compounds, thereby supporting the assumption of substantial charge localization of the carbanion across the ring in solvate 2. This is also reflected in the planarized carbanionic units around C1 and C8 ($\Sigma^{\circ}_{(C1)} = 357.6^{\circ}, \Sigma^{\circ}_{(C8)} =$ 360.0°). The solution-phase NMR spectrum reveals a single signal set for the benzyl moiety in 2, thus indicating that the asymmetric environment found in the crystal no longer exists in solution. The NMR chemical shifts of 2 in solution are consistent with a highly delocalized benzyl anion coordinating in a η^6 mode to the potassium counterion.^[17]

The structure of 1 poses the questions as to how closely it relates to the "classical" n-butyl LICKOR system which produced it in the first place and can it behave practically as a superbase itself? As Schlosser's base would be expected to initially produce PhK as the product,^[3] a partial post-metalation metal-metal exchange at least of PhK to PhLi must occur to allow for the formation of 1 as the most stabilized aggregate. As it contains all the fragments of a LICKOR base (hydrocarbon/Li/K/OtBu), aggregate 1 itself bears the hallmarks of a superbase. Consequently, the superbasic character of aggregate 1 was tested by its ability to metalate toluene. We were pleased to observe that the addition of toluene to crystalline 1 and warming to about -40°C resulted in the formation of BnK, thereby proving that 1 itself can indeed act as a "superbase" in the lateral metalation of toluene at low temperatures (Scheme 1).



Scheme 1. Top: Generation of 1 and 2 from LICKOR and simple arenes as well as the superbasic behavior of 1 towards toluene to generate 2. Bottom: Simplified structural motif of aggregate 1 (coordinated THF and benzene omitted) and possible (simplified) transition state for the metalation of toluene.

The structure of bimetallic cluster **1** reveals a number of four-membered Li-C-K-O rings as structural motifs (Scheme 1). In the literature, these "asymmetric aggregates" have often been linked to the increased reactivity of LICKOR base mixes compared to unimetallic organoalkali metal bases. Furthermore, this organopotassium-containing "outer ring" would be more accessible for metalation reactions than the inner organolithium core: The potassium centers each bear labile THF or η^1 -coordinating benzene ligands, which could easily be displaced by coordinating substrates, thus bringing them in proximity to the phenyl moieties for a subsequent metalation. A possible simplified transition state for the deprotonation of toluene by a bimetallic fragment comprising PhK and *t*BuOLi is shown in Scheme 2.

The computed energy barrier for the benzylic metalation is 75 kJ mol⁻¹ and is lower if the exchange of ligands in the potassium coordination sphere is taken into account. The calculations show that substitution of a η^1 -coordinating Me₂O donor for the toluene substrate is favored by 9 kJ mol⁻¹, thereby further lowering the energy barrier for metalation,



Scheme 2. Model for the deprotonation of toluene by **1**. Top: Energies for the ligand/substrate exchange and the subsequent metalation step in the model system. Bottom: Geometry of the corresponding transition state [M052X/6-31 + G(d)].

consistent with the experimental findings (ca. -40 °C) described above.

With the structure of the organometallic components in our THF reaction mixtures elucidated, we investigated the outcome of the remaining alkoxides. Further concentration of the mother liquors of reaction mixtures stemming from the metalation of benzene led to small crops of colorless crystals, typically after storage of the solution for several days at -78 °C. They were identified as cluster **3** (Figure 3). The bimetallic alkoxide cluster [(*t*BuOK)(*t*BuOLi)₄(THF)₃] (**3**) crystallizes from THF in the monoclinic crystal system in the space group *Cc*. Its metal scaffold is formed by a KLi₄ square pyramid. Each face is capped by a *tert*-butoxide anion (μ^3 in



Figure 3. Molecular structure of the alkoxide cluster by-products of the LiCKOR metalation in THF: Left: $[(tBuOK)(tBuOLi)_4(THF)_3]$ (3). Right: $[(tBuOLi)_4(THF)_4]$ subunit of **4** (hydrogen atoms omitted for clarity).

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the case of the KLi₂ triangles and μ^4 in the case of the Li₄ base). The apical potassium atom and two vicinal lithium centers are coordinated to an additional THF molecule. Another alkoxide cluster was characterized from the mother liquor of solutions which produced benzylpotassium 2: In this case, colorless crystals of lithium tert-butoxide THF solvate $[(tBuOLi)_8(THF)_7]$ (4) were obtained. The unimetallic alkoxide compound crystallizes in the orthorhombic crystal system in the space group $P2_12_12_1$. The asymmetric unit contains two tetrameric units of lithium tert-butoxide, each featuring a heterocubane structure with each butoxide group capping one Li3 face. Although each of the four lithium centers of the first unit is coordinated by a further THF molecule, only three lithium atoms of the second unit are coordinated to a THF molecule, thereby leaving one further free from the solvent. It is of interest to note that the bimetallic 1 gave rise to bimetallic by-product 3, whereas unimetallic 2 resulted in the isolation of unimetallic alkoxide 4.

In summary, we have successfully elucidated the structures of the metalated intermediates arising from the deprotonation of the two most elementary arenes benzene and toluene by using the LICKOR base nBuLi/tBuOK in THF, as well as the structure of the respective alkoxide cluster by-products. The nature of the deprotonated substrate dictates the structure-building principle and decides how the building blocks of "spent" LICKOR mixtures-carbanionic residue of the metalated substrate, alkoxide, lithium and potassium counterions-interact. The metalation of benzene results in a comparatively "hard" phenyl anion which assembles alongside an alkoxide moiety in the bimetallic, aggregate 1, which itself acts as a superbase, efficiently deprotonating toluene. In comparison, the soft, delocalized benzyl anion favors potassium as the counterion, and forms the unimetallic, polymeric organopotassium aggregate 2. In a bimetallic, molecular aggregate of type 1, the hard lithium cation provides an anchor for the anions, which keeps the size of the aggregate small and increases the solubility compared to extended polymeric aggregates. In contrast, the softer potassium cation makes the facile pre-coordination of substrates bearing π electrons possible. Thus, the bimetallic aggregate serves to precoordinate the toluene substrate for the subsequent, synergic metalation step of the superbasic assembly.

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