Superbases **Very Important Paper**

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Combining Neopentyllithium with Potassium *tert*-Butoxide: Formation of an Alkane-Soluble Lochmann–Schlosser Superbase

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In memory of Malcolm H. Chisholm

Abstract: *Mixtures of alkyllithium and heavier alkali-metal alkoxides are often used to form alkyl compounds of heavier alkali metals, but these mixtures are also known for their high reactivity in deprotonative metalation reactions. These organometallic mixtures are often called LiC–KOR superbases, but despite many efforts their constitution remains unknown. Herein we present mixed alkali-metal alkyl/alkoxy compounds produced by reaction of neopentyllithium with potassium tert-butoxide. The key to success was the good solubility and temperature-stability of neopentyl alkali-metal compounds, leading to hexane-soluble mixtures, which allowed handling at ambient temperatures and isolation by crystallization. The compounds in solid state and in solution were identified by X-ray crystallography and NMR spectroscopy as mixtures of lithium/potassium neopentyl/tert-butoxy aggregates of varying compositions* $Li_xK_yNp_z(OtBu)_{x+y-z}$.

Organometallic bases formed by the combination of alkyllithium compounds (LiC) with potassium alkoxides (KOR) are often referred to as LiC–KOR or Lochmann–Schlosser superbases (LS).[1] The term superbase was coined by Schlosser to emphasize the high reactivity and regioselectivity in hydrogen/metal exchange reactions, Caubère defines it as "new basic species possessing inherent new properties".[2] These mixtures with their metalating power of unreactive C–H bonds could demonstrate their usefulness in synthetic chemistry over the last five decades as an alternative to lithium compounds or Grignard reagents.[3] The mixture of alkyllithium compounds with potassium alkoxides[4] produces alkylpotassium.[5] The source of the extraordinary reactivity of such mixtures could be attributed to the alkylpotassium (KR) formed. However, the contribution of a potential intermediary mixed alkyl/alkoxy aggregate[6] $[LiK(OR')R]_n$ cannot be ruled out (Scheme 1).

$$n\,LiR + n\,KOR' \longrightarrow [LiKR(OR')]_n \rightleftharpoons n\,KR + n\,LiOR'$$

Scheme 1. Reaction of alkyllithium (LiR) with potassium alkoxide (KOR′) and formation of mixed aggregates, R = *n*Bu, neopentyl, R′ = *t*Bu.

A number of results point at a major or even exclusive role of the potassium compound formed.[7] Neither the precipitated alkyl potassium[5b,c] nor the products formed in reactions with organic substrates[8] show noteworthy amounts of lithium or alkoxide. The use of different alkoxides[9] or excess of alkoxide[10] had no significant influence on the products of the reaction. Spectroscopic examinations by NMR[11] or ESR spectroscopy[12] confirmed these findings. Studies based on ^{7}Li-^{1}H and ^{133}Cs-^{1}H HOESY NMR spectroscopy of a reaction of trityllithium ($LiCPh_3$) with cesium 3-ethyl-3-heptoxide also disproved the existence of mixed alkyl/alkoxy species.[7] On the other hand, there is also strong evidence for the formation of mixed alkyl/alkoxy species: influence of concentration[13] and structure[14] of potassium alkoxides used on reaction rates, improved thermal stability[15] of solutions in THF and differences in kinetic isotope effects.[16] The lack of structural information for mixed aggregates can be attributed to the low solubility and the tendency to undergo β-hydride elimination[17] of alkylpotassium, which removes it from the corresponding equilibrium (Scheme 1). However, a comparable tetrameric homo-metallic aggregate, $[Li_8(nBu)_4(OtBu)_4]$, was formed by mixing LiO*t*Bu with *n*-butyllithium. Its composition was determined both in solution by NMR spectroscopy[18] and in the solid state.[19] Another bimetallic model system for LS superbases is a crystalline 1:1 mixture of LiO*t*Bu and KO*t*Bu: $[Li_4K_4(OtBu)_8]$ (**1**),[20] which crystallizes in tetrameric units. The same structural motif was also found for the corresponding Li/Na, Li/Rb, and Li/Cs pairs.[21] Other bimetallic examples are the intramolecular combination of both a phenoxy and an alkyl group[22] and a superbasic mixed amido/alkoxy compound.[23] The recent successful isolation and structural characterization of the metalation product of benzene with the LS superbase in THF by Strohmann et al. afforded $[Li_2K_4(OtBu)Ph_5(THF)_6]$,[24] showing both the bimetallic nature and the corresponding metal–oxygen/metal–carbon interactions suggested for LS superbases.

To facilitate the formation of mixed aggregates of the composition of $Li_xK_yR_z(OtBu)_{x+y-z}$ by overcoming the obstacle of low solubility of alkylpotassium in alkanes,[25,26] we turned to the neopentyl group (CH_2tBu, Np). It promises better solubility and higher stability compared to *n*-butyl, a consequence of the absence of β-hydrogen atoms. Therefore we carried out a reaction between neopentyllithium,[27] LiNp, and KO*t*Bu[4] in *n*-hexane. The precipitate formed was collected by filtration, washed with *n*-hexane, and dried in vacuum. Although the resulting grayish and pyrophoric powder was poorly soluble in deuterated cyclohexane, it still could be identified by NMR spectroscopy as neopentylpotas-

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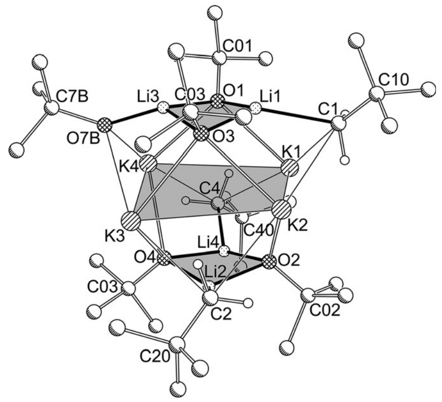


Figure 1. Molecular structure of **3** with selected atoms labeled and disordered units and *t*Bu-hydrogen atoms omitted for clarity. The NpLi(O*t*Bu)$_2$LiNp units and the central K$_4$ motif are shaded for emphasis.

sium (KNp, **2**). Two signals clearly could be attributed to resonances of the *tert*-butyl and the CH$_2$ groups, the CH$_2$ signal with a chemical shift of $\delta = -0.95$ ppm (compared to LiNp with $\delta = -0.62$ ppm in the same solvent).[28] Encouraged by the low yields of precipitated **2** of only 24% (compared to [KCH(SiMe$_3$)$_2$] and [KCH$_2$SiMe$_3$] with 80–90%),[25,26] we started to examine the filtrate for potassium compounds. Storing the solution at −30°C for several days afforded large colorless crystals, which were characterized by X-ray crystallography as mixed aggregate **3** with the approximate composition [Li$_4$K$_4$Np$_3$(O*t*Bu)$_5$]. Crystallizing in the orthorhombic space group *Pna*2$_1$,[28] it is isostructural to monoclinic [Li$_4$K$_4$(O*t*Bu)$_8$] (**1**).[20] However, several O*t*Bu groups are statistically replaced by Np (Figure 1).

Both compounds **1** and **3** are composed of a planar square of four potassium atoms [K$_4$]$^{4+}$, which is electrostatically coordinated from both sides by dianionic [RLi(O*t*Bu)$_2$LiR]$^{2-}$ units (R = O*t*Bu (**1**), CH$_2$*t*Bu (**3**)) in a staggered fashion relative to each other. The four lithium and four potassium atoms are arranged on the corners of a truncated tetrahedron, forming four LiK$_2$ triangles and four Li$_2$K$_2$ trapeziums, the triangles are capped mainly by Np groups, the trapeziums capped exclusively by O*t*Bu groups. Two different types of structural disorder complicated the structural refinement of compound **3**, based on the structural characteristics of the Np group (Figure 2). The four peripheral positions of the [RLi(O*t*Bu)$_2$LiR]$^{2-}$ units exhibit statistical substitutional disorder in an average Np/O*t*Bu ratio of approximately 2.75/1.25. The central O*t*Bu groups of the [Li(O*t*Bu)$_2$Li] units with the oxygen situated above a Li$_2$K$_2$ trapezium are not affected by this substitutional disorder, resulting in the approximate formula [Li$_4$K$_4$Np$_{2.75}$(O*t*Bu)$_{5.25}$]. This substitutional disorder is compounded by a conformational/positional disorder of the Np (and O*t*Bu) groups and potassium atoms; therefore the interatomic distances can only be approximations and will not be discussed in detail. However, the structural model is in good agreement with the X-ray crystallographic data, the molecular connectivity is conclusive. All four potassium atoms are disordered over two nearby positions in a 55/45 ratio, resulting in two planar K$_4$ squares rotated 11° against each other. The four Np groups (or the corresponding disordered O*t*Bu groups) are situated over LiK$_2$ triangles (Figure 2), illustrating the preference of the Np groups for μ$_3$ coordination. The two corresponding potassium atoms are forming one side of the disordered planar square K$_4$ substructure, resulting in a corresponding positional disorder of the attached groups.

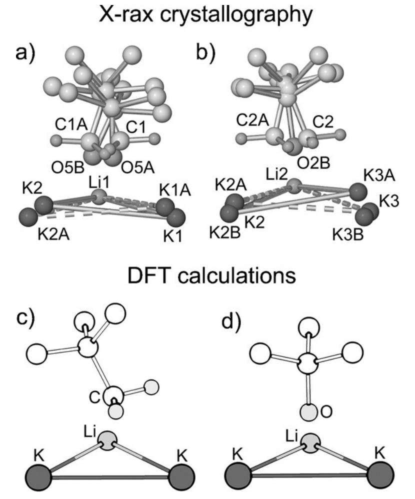
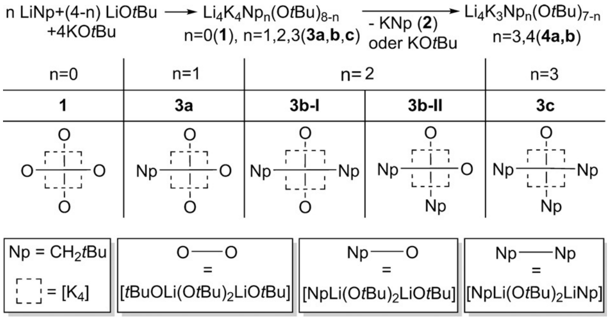


Figure 2. Modeling of substitutional and conformational disorder of potassium atoms, Np and O*t*Bu groups in molecular structures of **3** (a) and **4** (b). c),d) orientations of Np and O*t*Bu groups relative to LiK$_2$ arrangements as obtained by DFT calculations for compound **3a** in the gas phase.

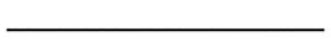
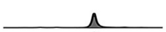
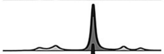
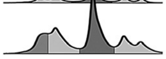
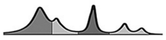
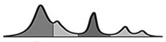
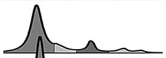
The structural similarity between compounds **1** and **3** and the substitutional disorder found in **3** did raise the question whether compound **1** could be enriched step-by-step with Np, resulting in compounds of the formula [Li$_4$K$_4$Np$_n$(O*t*Bu)$_{(8-n)}$], **3a** ($n = 1$), **3b** ($n = 2$), **3c** ($n = 3$), and **3d** ($n = 4$). A concentration series was carried out by adding increasing amounts of LiNp to a mixture of LiO*t*Bu and KO*t*Bu using *n*-hexane as solvent and isolating crystalline solids at −30°C (Scheme 2).

At low LiNp content (0.125 equiv), the two O*t*Bu ^{1}H NMR resonances of compound **1** at δ = 1.15 and 1.25 ppm were joined by additional resonances of **3a** (Table 1): one singlet at δ = 1.28 ppm for an additional O*t*Bu and two Np singlet signals at δ = 1.04 and −0.82 ppm, the δ = −0.82 ppm resonance is neither characteristic for the CH$_2$ groups of LiNp (δ = −0.62 ppm) nor for **2** (δ = −0.95 ppm, see above). The same hybrid tendency can be found for the corresponding ^{13}C resonance at δ = 44.3 ppm



Scheme 2. Schematic representation and formation of compounds **2**–**4**, by stepwise enrichment of compound **1** with Np groups.

Table 1: Concentration series with changing equivalents of added LiNp, KO*t*Bu, and LiO*t*Bu in *n*-hexane and determination of the composition of crystallized products by ^{1}H-NMR spectroscopy in [D$_{12}$]cyclohexane.

Equivalents of LiNp/KO*t*Bu/LiO*t*Bu	^{1}H-NMR[a] Np-CH$_2$ region	Np/O*t*Bu[b]	major/minor component
0:1.0:1.0		0:8	**1**
0.125:1.0:1.0		0.4:7.6	**1/3a**
0.25:1.0:1.0		0.9:7.1	**3a/3b(I+II)**
0.33:1.0:1.0		1.2:6.8	**3a/3b(I+II)**
0.5:1.0:1.0		1.6:6.4	**3b(I+II)/3c. 4**
0.66:1.0:1.0		1.9:6.1	**3b(I+II)/4. 3c**
0.75:1.0:1.0		2.3:5.7	**3c. 4/3b(I+II)**
1.0:1.0:1.0		3.0:5.0	**4/3c**
1.25:1.0:0.5		3.9:4.1	**4/3c**

[a] CH$_2$-Np region of ^{1}H NMR spectrum, $\delta = -0.65$ to -0.95 ppm.
[b] Ratio of the integral intensity of *t*Bu resonance signals of Np and O*t*Bu groups.

(LiNp: $\delta = 34.7$ ppm, and **2**: $\delta = 48.0$ ppm). Further addition of LiNp leads to further splitting of the O*t*Bu resonances and growth of the intensity of the Np resonances, which exceeds those of pure **2** in the same solvent. This and the detection of intramolecular interactions of Np and O*t*Bu groups with each other by ^{1}H-^{1}H-NOESY at higher LiNp content confirm the existence of mixed Np/O*t*Bu aggregates in solution. Already at low LiNp content a new feature becomes apparent: two doublet signals ($\delta = -0.74$ and -0.89 ppm) with a splitting of 11 Hz are found symmetrical to the central singlet at $\delta = -0.82$ ppm. This diastereotopic splitting of the Np-CH$_2$ group is caused by a resulting asymmetry of the present dineopentyl compound **3b-II** (Scheme 2).

Assuming the structure in solution is similar to the structure found in the solid state, the presence of two Np groups enables the formation of two isomers (Scheme 2): both Np groups can either be situated in the [NpLi(O*t*Bu)$_2$LiNp]$^{2-}$ unit above the [K$_4$]$^{4+}$ square (**3b-I**), or the two Np groups are spread between two different [NpLi(O*t*Bu)$_2$LiO^{t}Bu]$^{2-}$ units above and below the [K$_4$]$^{4+}$ square (**3b-II**). Both isomers and also the addition of a third (symmetric) Np group to form **3c** (also with two diastereotopic Np substituents) lead to a combination of singlet and diastereotopic doublets. This feature gets more prominent when increasing the amount of added LiNp to 0.5, 0.66, 0.75, and 1.0 equivalents, the *t*Bu of Np singlet can be observed at $\delta = 1.04$–1.05 ppm, while the O*t*Bu resonances broaden into a region from $\delta = 1.20$ to 1.35 ppm and the singlet at $\delta = 1.15$ ppm finally disappears. A broad signal slowly building up along the concentration series is observed at $\delta = -0.73$ ppm, it reaches a maximum intensity for a ratio of LiNp, KO*t*Bu, and LiO*t*Bu of 1.25/1/0.5. ^{1}H NMR spectra at 50 °C of solutions with low Np content show simply a broadening of the diastereotopic splitting, while high Np content on the other hand increases the intensity of the broad signal at $\delta = -0.73$ ppm. This suggests a higher thermal stability of compounds, such as **1**, **3a**, and **3b**, while higher Np content leads to structural instability of **3c** (and the absence of **3d** with four Np groups) at ambient temperature, leading to an equilibrium between two or more compounds. Cooling Np-rich solutions to −30 °C on the other hand produces two different NMR resonances (^{1}H: $\delta = -0.67$ and -0.86 ppm; ^{13}C: $\delta = 43.0$ and 47.7 ppm). From such solutions single crystals of **4** are obtained (Figure 3). The molecular structure derived from diffraction data reveals **4** (obtained from **3** by elimination of one KNp or KO*t*Bu unit), which is best described as the combination of a [Li$_4$(O*t*Bu)$_3$]$^+$ unit with a [K$_3$Np$_3$(OtBu)]$^-$ (**4a**) or a [K$_3$Np$_4$]$^-$ (**4b**) unit, both with two chemically different Np groups.

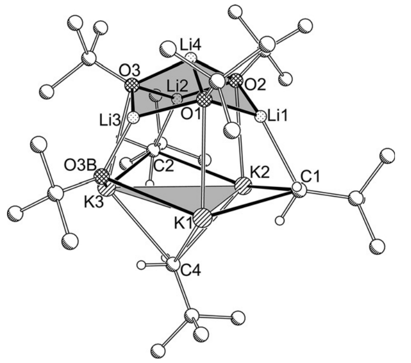


Figure 3. Molecular structure of **4** (represented as **4a**) with selected atoms labeled and minor disordered units and *t*Bu-hydrogen atoms omitted for clarity. The Li$_4$(O*t*Bu)$_4$ unit and the K$_3$ unit are shaded for emphasis.

These units combine to form a Li$_3$K$_3$ octahedron with opposing Li$_3$ and K$_3$ triangular faces. The Li$_2$K faces of the octahedron are capped by O*t*Bu groups (Li−O ranging from 1.941(4) to 1.966(4) Å), which also bind to the fourth lithium atom capping the Li$_3$ triangle (Li−O ranging from 1.869(4) to 1.890(4) Å). The potassium atoms are disordered because the three groups capping the LiK$_2$ triangles show substitutional disorder between O*t*Bu and Np, the Np also showing conformational disorder (Figure 2). Therefore all the distances and angles involving potassium will not be discussed in detail. The ratio between O*t*Bu and Np in these positions is 0.84/2.16, indicating a ratio between **4a**/**4b** of 0.84/0.16. The K$_3$ face is capped by a μ_3-bonded Np group showing conformational disorder over two positions. Despite the disorder of almost all the components involved, a common pattern emerges both in **3** and **4**, concerning the orientation of the Np groups μ_3-coordinated to the corresponding LiK$_2$ triangles. Considering the disordered units of major occupancy, the Li-C(CH$_2$)-C(*t*Bu) angles range from 113.8(9)° to 122.9(8)° in **3**, and from 119.6(6)° to 123.6(4)° in **4**, indicating a more covalent Li−C interaction. The corresponding K-C(CH$_2$)-C(*t*Bu) angles can be divided into two groups, with smaller (107.9(8)° to 111.2(7)° in **3**, and 105.6(6)° to 110.9(6)° in **4**) and larger angles (157.4(8)° to 166.3(9)° in **3**, and 154.4(4)° to 157.7(6)° in **4**). The two protons of the Np-CH$_2$ are directed symmetrically towards the potassium atoms involving the larger angles in an agostic type interaction, while the other potassium ion shows a merely electrostatic interaction. To clarify the bonding situation of Np and to explore the structural feasibility, we calculated the structures

1, **3a**, **3b(I + II)**, **3c**, **3d**, **4a**, and **4b** by density functional theory calculations (B3LYP/6-31G* level of theory)[29] in the gas phase. Using **3a** (Figure 2) as an example, the $\mathrm{LiK_2}$ triangle (Li−K 3.062 and 3.173 Å, K−K 3.980 Å) is μ_3-coordinated by the $\mathrm{CH_2}$-Np group (Li−C 2.206 Å, C−K 2.960 and 3.086 Å), the shorter C−K distance is combined with short K−H interactions of the $\mathrm{CH_2}$ group (2.673 and 2.703 Å). The Li-C($\mathrm{CH_2}$)-C(*t*Bu) angle (123.08°) and K-C($\mathrm{CH_2}$)-C(*t*Bu) angles (109.02° and 161.59°) are in good agreement with the average values found in the crystallographic measurements. The corresponding angles for O*t*Bu groups are more symmetrical relative to the potassium atoms (Li-O-C(*t*Bu) 135.77°, K-O-C(*t*Bu) 121.46° and 122.53°). The experimental structures of both compounds **3** and **4** show only weak intermolecular K⋯Me interactions, providing an explanation of their good solubility in alkanes.

In summary, this study comprehensively examined the formation of alkane-soluble and room-temperature-stable Lochmann–Schlosser superbases, which allow reactions in homogenous solutions at ambient temperatures. The studies both in solution and solid state confirmed the close interaction of lithium, potassium, alkyl, and alkoxy groups, and the deviation from ideal stoichiometry reflecting conceivable equilibria in solution. The formation of **2** and **3** from a 1:1 mixture of LiNp and KO*t*Bu points to an incomplete conversion (into LiO*t*Bu, KNp or its aggregates) with residual KO*t*Bu. Increasing the concentration of LiNp to more than one equivalent doesn't lead to the formation of **3d**, but to the formation of **4a** and the elimination of KNp (**2**) which itself is absorbed by excess LiO*t*Bu. The very unusual coordination of an alkyl group to both lithium and potassium in **3** and **4** leads to a hybrid Li/K−C bond polarity, which can be detected both in ^{1}H and ^{13}C NMR spectra. The electrophilic $\mathrm{LiK_2}$ platform offers two possible binding modes for reactions with nucleophilic substrates, Li for hard, and K for soft Lewis bases. These two principles, hybrid bond polarity and adaptable Lewis acidity uncovered in this study may explain the reactivity of such bases in organic synthesis.

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