Alkali metal complexes based on bisheterocyclomethanide ligands†‡†

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A series of new alkali metal complexes containing deprotonated bisheterocyclomethanide were synthesised and structurally as well as spectroscopically characterised. Starting from the neutral bis-(benzoxazol-2-yl)methane ([NCOC₆H₄]₂CH₂), the complexes were obtained by facile deprotonation of the methylene bridge with n-butyllithium (nBuLi) or potassium hydride. Each of the resulting complexes [[(NCOC₆H₄]₂CH)Li(OEt₂)]ₙ (1), [[(NCOC₆H₄]₂CH)K(thf)]ₙ (2) and [[(NCOC₆H₄]₂CH)K(18-crown-6)]ₙ (3) (n → ∞) was analysed in the solid state by single crystal X-ray diffraction and in solution by various NMR techniques. All the compounds show a nearly planar ligand with the alkali metal ion chelated by the two ring nitrogen atoms of the conjugated C₃N₂ moiety. Furthermore, water NMR titration experiments revealed that both compounds 2 and 3 are examples of water-stable reactive organo potassium compounds. Due to their hydrolysis stability, these complexes are under further investigations in deep eutectic solvents.

In 1975, one of the first examples with an unexpected influence of water on the outcome of an alkali organometallic reaction was published by Taylor. It was observed that the most convenient method for the synthesis of tritiated arenes was the addition of nBuLi to a bromoarene in T₂O wetted sodium-dried Et₂O. The formation of labelled arenes was explained by a lithium/bromide exchange reaction that has to be at least as fast as, and most probably even faster than, the expected reaction between nBuLi and T₂O.5

Another landmark was the lithiation of 2-mercaptopbenzoxazole in the presence of N,N,N’,N’-tetramethylethylenediamine (TMEDA) and H₂O and was reported by Wright and co-workers. The obtained complex [[C₆H₄OCSN)Li(TMEDA)H₂O] shows a strong hydrogen bonding between one proton of a coordinated H₂O molecule and the polarised sulfur atom of the anion rather than a protonated Li–OH⋯SH species.5 In 1992, Schleyer et al. presented the crystal structure of a lithium H₂O-containing complex of an organic molecule bearing an acidic C–H unit. The addition of TMEDA and H₂O to lithiated malonodinitrile in a 1:1:1 molar ratio led to the formation of [Li(CH(CN))₂H₂O] [TMEDA]ₜₜ. This polymeric structure includes some interesting features e.g. the lack of TMEDA–Li interactions which is unprecedented for a bidentate ligand as well as the ability of each H₂O molecule to simultaneously mould hydrogen bonding to TMEDA (donor function) and lithium ions (acceptor function).1–3 Recently we found ([18-crown-6]K[(4,6-Bu-OCNC₆H₄]CH]H₂O) as a water-containing organopotassium complex based on the bulky deproto-
nated bis(4,6-tBu-benzoxazol-2-yl)methane. Its crystal structure revealed a rare example of a bis(benzoxazole-2-yl)methanide featuring solely O-coordination to a potassium ion. Furthermore, its unparalleled water-stability was investigated by NMR titration and DOSY spectroscopy. The complex shows full protonation only after seven days and 114 equivalents of water and might turn out to be a sustainable synthetic synthon in deep eutectic solvents.7,8

In this paper, the preparation of one organolithium and two organopotassium compounds is presented. All complexes reported herein were characterised by single crystal X-ray diffraction. Additionally, the potassium complexes were tested for hydrolysis stability and monitored by NMR experiments.

Results and discussion

Synthesis and characterisation of [[(NCOC6H4)2CH)Li(OEt2)2] (1)

Following similar protocols to those of Stalke9 and Roesky10 [[(NCOC6H4)2CH)Li(OEt2)2] (1) was prepared by facile deprotonation of bis-[benzoxazol-2-yl)methane with nBuLi in diethyl ether (Et2O) at 0 °C (Scheme 1). Once the addition of nBuLi solution was complete the reaction mixture was stirred for 2 h and the lithiated species was grown from a saturated Et2O solution at 2 °C. It crystallises in the monoclinic space group P21/c with one molecule in the asymmetric unit. Mononuclear [[(NCOC6H4)2CH)Li(OEt2)2] (1) (Fig. 1) consists of a lithium ion which is N,N-chelated by the negatively charged ligand and two diethyl ether molecules in a distorted tetrahedral fashion. The two imine nitrogen atoms of the bis-[benzoxazol-2-yl)methanide coordinate the metal ion equidistantly (1.995(2) Å for Li(1)1.995(2) Å for Li(1) and 2.004(2) Å for Li(1)−N(2)). The bite angle N(1)−Li(1)−N(2) of 94.1(1)° is much more acute than the ideal tetrahedral angle. The oxygen atoms of the diethyl ether molecules coordinate at Li(1) in distances of 1.980(2) Å (Li(1)−O(3)) and 1.978(2) Å (Li(1)−O(4)), respectively. The included O(3)−Li(1)−O(4) angle of 103.0(1)° is much wider than the aforementioned angles. The nacnac-like planar structural C3N2 unit in [[(NCOC6H4)2CH)Li(OEt2)2] (1) shows bond lengths between 1.54 Å (C(sp2)−C(sp3)) and 1.34 Å (C(sp3)−C(sp3)) as well as between 1.47 Å (C(sp3)−N(sp3)) and 1.29 Å (C(sp3)−N(sp3)), indicating a fully conjugated system extended throughout the virtually planar ligand.11

The lithium ion is only 0.050(3) Å dislocated from the central chelating C3N2 plane. This almost ideal in-plane arrangement is also observed in [[4,6-iPr-NCOC6H4)2CH)Li(thf)2]12 (0.00(3) to 0.07(5) Å). Furthermore, a butterfly folding angle of 8.04(3)° between both benzoxazole moieties indicates only a slightly bent ligand system. In addition, complex 1 was analysed by NMR spectroscopy. The 7Li NMR spectrum shows a signal at 2.19 ppm (thf-d8) which suggests the formation of a single lithium complex in solution. The 1H NMR spectrum of complex 1 reveals that in contrast to the uncharged ligand a de-shielding and simultaneous downfield shift from the methane to the methanide bridge from δ–(H2C−) = 4.70 ppm to δ−(H2C−) = 4.80 ppm occurs. The aromatic protons experience an up-field shift. This correlates with an increased electron density at these atoms due to charge delocalization from the C3N2 bridge towards the aryl systems in the ligand periphery and indicates mainly σ-bonding of the lithium cation to the electron-rich imine atoms.11

![Scheme 1] Synthesis of [[(NCOC6H4)2CH)Li(OEt2)2] (1) by deprotonation with nBuLi solution in Et2O.
Synthesis and characterisation of potassium complexes 2 and 3

The syntheses of the closely related organopotassium compounds \([({NCOC_6H_4}_2CH)K(thf)]_n\) (2) and \([({NCOC_6H_4}_2CH)K(18\text{-crown-6})]_n\) (3) (Scheme 2) can be achieved in a clean reaction of bis-(benzoxazol-2-yl)methane with potassium hydride. The deprotonation at the acidic methylene bridge indicated by the release of hydrogen and coordination of a potassium ion starts already at \(-30^\circ\text{C}\). In the case of complex 2 thf was used as solvent, while the synthesis of 3 was conducted in toluene. Both reaction mixtures were allowed to warm to ambient temperature and stirred for about one day. After filtration and evaporation of all volatiles, both complexes were obtained as powders in good yields.

Solid-state structures of potassium complexes 2 and 3

Crystals suitable for single crystal X-ray diffraction were grown from a concentrated solution of the related solvents. \([({NCOC_6H_4}_2CH)K(thf)]_n\) (2) formed yellowish crystalline needles in the orthorhombic space group \(Pna\overline{2}_1\) with one molecule in the asymmetric unit. It forms polymeric zig-zag strands with potassium ions \(\text{N}_2\text{N}-\sigma\)-coordinated in the plane of one ligand and \(\eta^5\text{C}_3\text{N}_2\pi\)-coordinated to a second one (Fig. 2). In addition, each potassium cation is coordinated to a \(\mu\)-bridging thf molecule.\(^{14}\) Due to the formation of a conjugated \(\pi\)-system and the re-hybridisation of the carbon atoms at the methylene bridge from sp\(^3\) to sp\(^2\) upon deprotonation, a decrease in C–C bond lengths from 1.489(2) Å in the uncharged ligand \([({NCOC_6H_4}_2CH}_2\text{CH})\]\(^{15}\) to 1.403(3) Å in C(8)–C(9) and C(7)–C(8) is observed. The opposite is true for the distances between N(1)–C(7) (1.318(2) Å) and N(2)–C(9) (1.324(2) Å), which elongate in comparison with the bis-(benzoxazol-2-yl)methane (1.286(2) Å).\(^{15}\) To facilitate the \(\eta^5\)-coordination to a second ligand, the metal ion experiences a strong deviation of 0.784(3) Å from the coordinating C\(_3\)N\(_2\) plane that was also shown for the corresponding potassium in the complex \([([4\text{-MeNCOC}_6\text{H}_4}_2\text{CH})\]K(thf)] (1.33 Å).\(^{16}\) Structural features like the K–N distances (2.754(2), 2.762(2) Å) and the N–K–N bite angle (68.35(5)°) as well as the butterfly folding angle (7.25(7)°) between both benzoxazole moieties and best O(1)–N(1)–C(1–7) planes in regard to O(2)–N(2)–C(9–15) are also almost identical to those of \([([4\text{-MeNCOC}_6\text{H}_4}_2\text{CH})\]K(thf)].

\([([NCOC_6H_4}_2\text{CH})\]K(18-crown-6)]_n\) (3) forms pale yellow crystalline needles in the orthorhombic space group \(Pca\overline{2}_1\) with one molecule in the asymmetric unit. Its solid-state structure shows the formation of a molecular contact ion pair (Fig. 3).
Due to the high affinity of potassium to 18-crown-6 all six oxygen atoms of the crown coordinate to the cation. Additionally, a slipped $\eta^1$-C$_2$N$_2$ $\pi$-coordination of the anionic ligand is formed to one side of the embraced metal, while the other is $\eta^2$-coordinated to a benzyl moiety of an adjacent ligand, on this part already $\eta^3$-C$_2$N$_2$ $\pi$-coordinated to another carbazone. In the $\pi$-coordination, the N(2)-C(9) bond is closer to the metal than the opposite N(1)-C(7) bond. Additionally, both positions are N/O disordered. In the closer N(2)/O(2)-C(9) residue (K(1)-N(2) 2.87(2), K(1)-O(2) 3.0(1) Å) the nitrogen has a much higher occupancy of 0.82(3) relative to only 0.18(3) oxygen, while in the far N(1)/O(1)-C(7) moiety (K(1)-N(1) 3.37(9), K(1)-O(1) 3.42(5) Å) the oxygen occupies 61(3)% of the site. In $[(\text{NCOC}_6\text{H}_4\text{CH})\text{K}(18\text{-crown-6})]_n$ (3) the potassium metal is in demand of the much better donor nitrogen$^{17}$ different to the similar complex $[(\text{4,6-Bu-NCOC}_6\text{H}_4\text{CH})\text{K}(18\text{-crown-6})\cdot\text{H}_2\text{O}]^8$ in which the metal is exclusively oxygen coordinated. In the latter, an additional lattice thf molecule provides density to the metal which is much more beneficial than the $\eta^2$-coordination to the adjacent benzyl moiety in 3. Additionally, the rotation about the C-C bond in 3 is much facilitated because the benzoazolyl group is not further substituted. The rotation about the C-C bond in 3 is much facilitated because the benzoazolyl group is not further substituted. The rotation about the C-C bond in 3 is much facilitated because the benzoazolyl group is not further substituted. The rotation about the C-C bond in 3 is much facilitated because the benzoazolyl group is not further substituted.

NMR spectroscopic and hydrolysis studies of 2–3

The $^1$H NMR spectra (thf-d$_8$) of complexes 2 and 3 (ESI$^+$) show a set of signals in the aromatic region from 7.06 to 6.57 ppm which can be assigned to 2-H to 5-H as well as 11-H and 14-H of the $[(\text{NCOC}_6\text{H}_4\text{CH})\text{CH}]$ ligand. These signals are shifted up-field in comparison with 7.69–7.27 ppm of the aromatic protons of the free uncharged $[(\text{NCOC}_6\text{H}_4\text{CH})_2\text{CH}]$ ligand. In particular, 2-H and 14-H experienced a significant deshielding that leads to a down-field shift of 7.03–7.01 ppm (2) and 7.06–7.03 ppm (3), respectively. In addition, the $^1$H NMR spectra of compounds 2 and 3 reveal that in relation to the protonated $[(\text{NCOC}_6\text{H}_4\text{CH})_2\text{CH}]$ a slight shielding and up-field shift of the methanide bridge $\Delta\delta = 0.60$ ppm ($\delta(\text{CH})$) = 4.64 ppm, $\delta(\text{H}-\text{C})$ = 4.70 ppm) is observed. Furthermore, multiplets which can be assigned to the thf molecules of $[(\text{NCOC}_6\text{H}_4\text{CH})\text{CH}(\text{thf})]_n$ (2), occur at 4.64 ppm (O–CH$_2$) and 1.77 ppm (–CH$_2$). In contrast, the methylene functions of 18-crown-6 in 3 are observed at 3.46 ppm, which fits the chemical shift of related compounds.$^{19}$ Fuelled by the unexpected stability of $[(\text{4,6-Bu-NCOC}_6\text{H}_4\text{CH})\text{CH}(\text{18-crown-6})\cdot\text{H}_2\text{O}]$ towards hydrolysis we embarked on $^1$H NMR water titration experiments for compounds 2 and 3. Well-defined amounts of water (0.2 to 0.8 µL; 0.18 to 7.21 eq.) were added to a NMR sample and the effect of the successively increasing water content was monitored by $^1$H NMR spectroscopy. Both complexes $[(\text{NCOC}_6\text{H}_4\text{CH})\text{CH}(\text{18-crown-6})]$ (3) (ESI$^+$) and particularly surprisingly $[(\text{NCOC}_6\text{H}_4\text{CH})\text{CH}(\text{thf})]$ (2) are stable towards hydrolysis. Here the umbrella effect against hydrolysis recently observed by Gimbert et al. by complexing the lithium amide of 3-amino-pyrrolidine with lithium halides or MeLi cannot be operational.$^{20}$ It is shown in Fig. 4 that the addition of a vast excess of water has virtually no effect neither on the chemical shifts nor the signal line shape of complex 2. The water signal is first observed at 2.99 ppm (0.2 µL, 0.18 eq.) while shifting to 2.86 ppm (2.0–2.4 µL, 1.80–2.16 eq.). Even after adding 7.21 equivalents of water and waiting for one week still no protonation of 2 and formation of bis-(benzoxazol-2-yl)methane were detected. A slight deshielding and shift of 2-H and 14-H towards the down-field of $\Delta\delta = 0.06$ ppm can be observed. Due to $^1$H NMR water titration experiments of 2 and 3, these compounds seem to be interesting examples of water-stable organopotassium compounds. Apparently the $pK_a$ of the ligand is on par with that of water. This is why the $pK_a$ values in this ligand family are of urgent interest and will be determined soon. Further experiments to exploit the reaction behaviour of alkali metal bis-(benzoxazol-2-yl)methanide complexes are on the way.

Conclusions

In this work the successful syntheses of three alkali metal bis-(benzoxazol-2-yl)-methanides 1–3 are presented. These complexes were obtained by the concerted deprotonation-metallation reaction of bis-(benzoxazol-2-yl)methane with typical alkali–metal reagents such as nBuLi or KH. Each of the resulting complexes $[(\text{NCOC}_6\text{H}_4\text{CH})\text{Li(OEt)}_2]_3$ (1), $[(\text{NCOC}_6\text{H}_4\text{CH})\text{CH}(\text{thf})]_n$ (2) and $[(\text{NCOC}_6\text{H}_4\text{CH})\text{CH}(\text{18-crown-6})]$ (3) ($n \rightarrow \infty$) was characterised in the solid state by X-ray single diffraction and in solution by different NMR techniques. It was shown by $^1$H NMR water titration experiments that both organopotassium complexes 2 and 3 show surprising stability against hydrolysis. All complexes can be used as precursors for salt elimination and transmetallation reactions. Due to their hydrolysis stability, these complexes are under further investigations in deep eutectic solvents.
Experimental

General procedures

All reactions were carried out under an atmosphere of N2 and Ar by Schlenk techniques.21 All solvents were distilled from Na or K before using for synthesis. Starting materials were purchased commercially and used without further purification. 1H, 13C NMR spectroscopic data were recorded on a Bruker Avance 400 MHz and a Bruker Avance 300 MHz spectrometer and referenced to the deuterated solvent (thf-d8). Deuterated solvents were dried over activated molecular sieves (3 Å) and stored in an argon dry box. Elemental analyses (C, H, N) were carried out on a Vario EL3 at the Mikroanalytisches Labor, Institut für Anorganische Chemie, University of Göttingen. LIFDI-MS spectra were measured on a Jeol AccuTOF spectrometer.

Crystal data for 1 at 100(2) K: C23H32Li+N2O4, Mr = 404.42 g mol\(^{-1}\), 0.467 × 0.352 × 0.265 mm, monoclinic, P2\(_1\)/c, a = 17.284(3) Å, b = 9.722(2) Å, c = 13.883(2) Å, β = 97.03(2)°, V = 2208.1(8) Å\(^3\), Z = 4, μ(Mo Kα) = 0.082 mm\(^{-1}\), θmax = 25.547°, 24,547 reflections measured, 4129 independent (Rint = 0.0271), R1 = 0.0334 [{I > 2σ(I)}], wR2 = 0.0816 (all data), res. structure peaks: 0.210 to ≤−0.155 e Å\(^{-3}\).

Crystal data for 2 at 100(2) K: C19H17KN2O3, Mr = 360.44 g mol\(^{-1}\), 0.364 × 0.177 × 0.126 mm, orthorhombic, Pn2\(_1\)\(_1\)\(_2\)\(_1\)\(_1\), a = 12.200(2) Å, b = 19.897(3) Å, c = 7.745(2) Å, V = 1725.9(6) Å\(^3\), Z = 4, μ(Mo Kα) = 0.328 mm\(^{-1}\), θmax = 26.119°, 26,470 reflections measured, 3432 independent (Rint = 0.0238), R1 = 0.0210 [{I > 2σ(I)}], wR2 = 0.0566 (all data), absolute structure parameter 0.04(1),22 res. density peaks: 0.184 to ≤−0.250 e Å\(^{-3}\).

Crystal data for 3 at 100(2) K: C22H27KN2O6, Mr = 552.65 g mol\(^{-1}\), 0.226 × 0.172 × 0.098 mm, orthorhombic, Pn2\(_1\)\(_1\)\(_2\)\(_1\)\(_1\), a = 15.913(3) Å, b = 10.981(2) Å, c = 15.309(3) Å, V = 2675.1(9) Å\(^3\), Z = 4, μ(Mo Kα) = 0.251 mm\(^{-1}\), θmax = 26.427°, 33,321 reflections measured, 5489 independent (Rint = 0.0478), R1 = 0.0343 [{I > 2σ(I)}], wR2 = 0.0727 (all data), absolute structure parameter 0.01(2),22 res. density peaks: 0.288 to ≤−0.268 e Å\(^{-3}\).

Shock cooled crystals were selected from a Schlenk flask under an argon atmosphere using the X-TEMP2 device.23 The data were collected with an Mo Kα microfocus source.24 All data were integrated with SAINT25 and a multiscan absorption correction (SADABS)26 was applied. For structure 2, a 3λ correction was applied.27 The structures were solved by direct methods (SHELXT)28 and refined on F\(^2\) using the full-matrix least-squares methods of SHELXL29 within the SHELXL GUL30. The Crystallographic Information Files (CIF) using the reference numbers 1839909, 1839910 and 1839911.

\[\text{[(NCOC}_{3b}^h\text{H}_{4}^b)^{+}\text{CH}]K(\text{thf})}\] (2)

Bis-(benzoxazol-2-y1)methane (49.3 mg, 197 µmol, 1.00 eq.) was dissolved in thf (4 mL) and cooled to −30 °C. At this temperature potassium hydride (15 mg, 374 µmol, 1.90 eq.) was added. While stirring, the reaction mixture was warmed to room temperature. After 18 h, the solution was filtered, and solvents were removed under reduced pressure. Crystals from the yellowish solid (55 mg, 191 µmol, 97%) were grown from a concentrated solution of 2 in thf. 1H NMR (300 MHz, thf-d8, ppm): 7.03–7.01 (m, 2 H, 2-H, 2-H), 7.00–6.97 (m, 2 H, 3-H, 3-H), 6.84–6.79 (m, 2 H, 4-H, 12-H), 6.71–6.65 (m, 2 H, 4-H, 12-H), 4.64 (s, 1 H, 8-H), 3.62 (m, 4 H, O-CH2 thf), 1.77 (m, 4 H, CH2 thf), 13C NMR (75 MHz, thf-d8, ppm): 170.94 (C-7, C-9), 150.53 (C-6, C-10), 147.86 (C-1, C-15), 122.69 (C-3, C-13), 118.61 (C-4, C-12), 113.29 (C-2, C-14), 107.76 (C-5, C-11), 68.40 (O-CH2 thf), 56.98 (C-8), 26.55 (CH3 thf); MS (LIFDI\([+\], toluene): m/z = 249.0 (11) [M – K – thf]\(^−\), 288.0 (100) [M – thf]\(^−\), 327.0 (28) [M + K – thf]\(^−\]; a satisfactory CHN analysis could not be obtained because the coordinating thf leaves the lattice and gave varying not reproducible results.

\[\text{[(NCOC}_{3b}^h\text{H}_{4}^h)^{+}\text{CH}]K(18\text{-crown-6})}\] (3)

Bis-(benzoxazol-2-y1)methane (100 mg, 400 µmol, 1.00 eq.) was dissolved in toluene (5 mL) and cooled to −30 °C. At this temperature potassium hydride (24 mg, 600 µmol, 1.50 eq.) was added. While stirring, the reaction mixture was warmed to room temperature. After 24 h, the solution was filtered, and solvents were removed under reduced pressure. Crystals suitable for X-ray diffraction were grown from a concentrated solution of 3 (181 mg, 328 µmol, 82%) in toluene. 1H NMR (300 MHz, thf-d8, ppm): 7.06–7.03 (m, 2 H, 2-H, 2-H), 6.98–6.96 (m, 2 H, 5-H, 11-H), 6.80–6.75 (m, 2 H, 5-H, 11-H), 6.62–6.57 (m, 2 H, 4-H, 12-H), 4.64 (s, 1 H, 8-H), 3.46 (m, 24 H, 18-crown-6); 11C NMR (75 MHz, thf-d8, ppm): 170.74 (C-7, C-9), 151.06 (C-6, C-10), 148.35 (C-1, C-15), 122.41 (C-1, C-15), 117.41 (C-4, C-12), 114.06 (C-2, C-14), 107.12 (C-5, C-11), 70.91 (18-crown-6), 57.34 (C-8); MS (LIFDI\([+\], toluene): m/z = 303.1 (100) [M – [(NCOC}_{3b}^h\text{H}_{4}^h)^{+}\text{CH}]\); MS (ESI\([+\], thf): m/z = 303.1 (100) [M – [(NCOC}_{3b}^h\text{H}_{4}^h)^{+}\text{CH}]\); MS (ESI\([–\], thf): m/z = 249.1 (100) [M – K @18-crown-6]; 513.2 (12) [M – K]\(^−\), 521.2 (21).
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[|][|]; |H⁻|33|KN|2|O|2ː |C| 56.86; |H| 6.02; |N| 5.07%; |found| C| 56.96; |H| 5.65; |N| 5.70%.

Conflicts of interest

The authors declare no competing financial interest.

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Notes and references


