Sodium and Potassium Complexes of Anionic N-Heterocyclic Carbenes

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Dedicated to Prof. Dr. Christoph Janiak on the occasion of his 60th birthday.

The reaction of 1,3-bis(2,6-disopropylphenyl)imidazolin-2-ylidene (IDipp) with n-BuLi in the presence of sodium and potassium bis(trimethylsilyl)amide was studied, and the resulting polymeric dicarbene species were reacted with the fluoroboranes tris(pentafluorophenyl)borane, B(C$_6$F$_5$)$_3$, and tris[3,5-bis(trifluoromethyl)phenyl]borane, B(m-X$_2$F$_3$)$_3$, to produce sodium and potassium salts of an anionic N-heterocyclic carbene with a weakly coordinating borate moiety (WCA-NHC).

**Introduction**

The advent of modern organometallic chemistry in the middle of the 20th century had been sparked by the discovery and structural elucidation of bis(cyclopentadienyli)iron (ferrocene).[1] Ever since, cyclopentadienyl (Cp) derivatives have been among the most prominent ligands in transition metal as well as main group element chemistry,[2] including alkali metal complexes as the preferred transmetalation reagents.[3] The isolation and structural characterization of the first N-heterocyclic carbenes (NHCs) is arguably a similar important discovery,[4] which has made NHC ligands ubiquitous and indispensable in diverse research areas such as homogeneous catalysis,[5] medicinal chemistry,[6] and materials chemistry.[7] Nowadays, NHC complexes cover almost the whole periodic table of the elements, including the alkali metals despite the generally overall neutral charge of NHCs.[8] Early examples also appear to be used as transmetalation agents.[8] Numerous lithium salts have become available via the “anionic dicarbene” II,[10] which can be functionalized in the C4-position by treatment with electrophiles.[10,11] In our hands, the reaction with B(C$_6$F$_5$)$_3$ afforded solvated lithium complexes of type III (solv. = THF, toluene) containing carbenes with a weakly coordinating fluoroborate moiety, so-called WCA-NHCs, which have been used extensively for the synthesis of transition metal complexes and homogeneous catalysts,[12,13] and more recently, also for the preparation of main group element compounds.[14] In general, such anionic N-heterocyclic carbenes should be particularly suitable for synthesizing unusual alkali metal carbene complexes.[15]

In contrast to lithium, complexation of stable carbenes with heavier alkali metals is rare, and only a comparatively small number of well characterized sodium and potassium NHC complexes have been reported so far.[16] A remarkable exception are bis(NHC) complexes of the type [(iDipp)$_2$][M][M’[N-(SiMe$_3$)$_3$]] (IV: M = Na, K; M’ = Mg, Ca, Sr), which were obtained by combining equimolar mixtures of group 1 and group 2 bis(trimethylsilyl)amides with two equivalents of 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (iDipp).[16] Complexes related to this study have been obtained by alkali-metal-mediated magnesiation,[17] zincation,[18] and ferration[16] reactions or by treatment of IDipp with NaR and KR followed by addition of...
GaR₃ (R = CH₃SiMe₃). Selected examples V and VI are shown in Figure 1. These reactions involve polymeric sodium or potassium species similar to II, and a potassium salt with bridging K(THF)₂ units could be structurally characterized and used for the preparation of zinctated and stannylated NHC potassium complexes. Furthermore, potassium salts of abnormal NHCs could be generated by C₄-metallaion of imidazolium salts with n-butyl lithium (n-BuLi) and potassium bis(trimethylsilyl)amide (KHMDMS, HMDMS = hexamethyldisilazide).

Owing to our ongoing interest in exploiting the chemistry of WCA-NHC complexes, we aimed at the preparation of sodium or potassium bis(trimethylsilyl)amides together with the fluoroboranes tris[pentafluorophenyl]borane, B(C₆F₅)₃, and tris[3,5-bis(trifluoromethyl)phenyl]borane, B(m-XyF)₃. An initial account of these studies is given below.

Results and Discussion

Synthesis and Characterization of a Sodium Carbene Complex

The carbene DIipp was suspended in diethyl ether and treated with equimolar amounts of NaHMDS dissolved in THF and n-BuLi (1.6 M solution in n-hexane). After stirring at room temperature for 24 h, the resulting precipitate was filtered off, washed with n-hexane and dried under high vacuum. Because of its insolubility, the precipitate was used without further characterization, assuming the formation of a polymeric sodium salt in analogy to II with the fluoroborates tris(pentafluorophenyl)borane, B(C₆F₅)₃, and tris[3,5-bis(trifluoromethyl)phenyl]borane, B(m-XyF)₃. An initial account on these studies is given below.

Attempts to isolate a potassium complex analogous to 1 proved more difficult. It has been noted previously that the use of sodium or potassium bis(trimethylsilyl)amides together with n-BuLi for the deprotonation of DIipp is complicated by the generation of LHMDS. In our hands, the reaction of DIipp with KHMDMS and n-BuLi was performed in diethyl ether (with a small amount of THF), affording a colorless precipitate. Elemental analysis suggested the formation of a polymeric complex [K(THF)₃][DIipp] (2, x = 1, Scheme 2), while the crystal structure has been reported for x = 2. Single crystals were obtained by diffusion of n-hexane into a concentrated THF solution of the isolated precipitate, and X-ray diffraction analysis afforded the molecular structure of the mixed lithium-potas-

![Figure 2. ORTEP diagram of 1 with thermal displacement parameters drawn at 50% probability; the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Na–C1 2.5079(17), Na–O1 2.2823(16), Na–O2 2.3737(15), Na–O3 2.3291(15), B1–C2 1.646(2), N1–C1–N2 102.70(13), C1–Na–O1 132.18(6), C1–Na–O2 126.00(6), N1–C1–Na 133.40(11), N2–C1–Na 123.56(11), O1–Na–O2 85.34(6), O1–Na–O3 89.63(6), O2–Na–O3 106.79(6).]
sium complex 3 (Figure 3). 3 crystallizes in the monoclinic space group $P2_1/n$ and reveals one-dimensional chains, in which bis(carbene) potassium units are bridged by Li(THF) via the deprotonated carbene backbone. The potassium atom is primarily bound to the carbene carbon atoms with $K$–$C_1$ = 2.8394(14) Å and $K$–$C_{28}$ = 2.9045(14) Å and completes its coordination sphere by interaction with the ipso- and ortho-carbon atoms of the Dipp substituents. These potassium-carbon contacts range from 3.0839(16) to 3.6019(15) Å and are typical for potassium-$\pi$-aryl contacts.\textsuperscript{24} As a result, the carbene ligands are strongly tilted, which is indicated by very different $K$–$C$–$N$ angles, e.g., $K$–$C_1$–$N_1$ = 105.34(8)° and $K$–$C_1$–$N_2$ = 151.35(10)°.

In contrast to bis(NHC) potassium complexes of type IV,\textsuperscript{16} the $C_1$–$K$–$C_{28}$ angle of 128.57(4)° shows a cis rather than a typical trans arrangement of the NHC units. The lithium ion adopts a distorted trigonal-planar geometry and is bound to one THF ligand with $Li$–$O$ = 1.985(3) Å and to the carbene backbone with $Li$–$C_2$ = 2.092(3) Å and $Li$–$C_{29}$ = 2.097(3) Å, which is shorter than reported for the related complex $II$·THF, viz. $Li$1–$C_1$ = 2.175(6) Å and $Li$1–$C_{30}$ = 2.125(6) Å.\textsuperscript{10}

Treatment of the lithium-potassium complex 3 with two equivalents of the borane $B(C_6F_5)_3$, in toluene afforded the complex [Li(THF)][(WCA-IDipp),]·THF (4) after recrystallization from THF/n-hexane solution. The $^1H$ NMR spectrum (in THF-$d_8$) shows the characteristic signals for the backbone CH hydrogen atoms at 6.13 ppm; the $^{13}$C($^1H$) NMR resonance of the carbene carbon atom is found at 217.4 ppm. Crystals of 4·THF suitable for X-ray crystal structure analysis were obtained at room temperature by diffusion of $n$-hexane into a concentrated THF solution. The molecular structure was refined as a racemic twin (with a twin ratio of 43 to 57%) in the triclinic space group $P1$ (Figure 4). While the isolation of 4 is in agreement with the formation of the intermediate 3, it should be noted that single crystals of the pure potassium complex [K(THF)] [(WCA-IDipp),]·THF (5) were isolated on another occasion, albeit not in a reproducible fashion, suggesting 2 as the more likely intermediate. 5·$n$-
hexane crystallized in the triclinic space group $P\overline{1}$, and the molecular component is shown in Figure 5. In both complexes 4 and 5, the anionic components each consist of a centrosymmetric $\{\text{WCA-IDipp}\}K^+$ ion, which displays structural parameters very similar to those established for the cationic parts in the complexes $\{\text{IDipp}\}_K\{\text{M(NSiMe$_3$)$_2$}$_2\}$ ($\text{M} = \text{Mg, Ca, Sr, Ba}$) of type IV (Figure 1). Thus, the potassium-carbene distances of 2.828(4)/2.852(4) Å in 4 and 2.9080(12) Å in 5 fall in the same range (2.8210(2)–2.8614(17) Å), and the coordination is augmented by the same asymmetric $\eta^1$-interaction with the ipso- and ortho-carbon atoms of the Dipp substituents adjacent to the borate moiety ($C_{\text{phen}}$ distances ca. 3.19 Å, $C_{\text{ortho}}$ distances ca. 3.31–3.43 Å). In contrast to 3, the C–C–K angles of 179.19(16)$^\circ$ (4) and 180$^\circ$ (5) reveal a linear arrangement of the two WCA-NHC ligands, with the additional $z$-interaction affording a strong inclination and very different K–C–N angles, see K–C1–N1 = 107.85(8)$^\circ$ and K–C1–N2 = 147.63(8)$^\circ$ in 5.

The reaction of the solid obtained from the reaction of IDipp with KHMDS/n-BuLi (presumably a mixture of 2 and 3) was also treated with tris[3,5-bis(trifluoromethyl)phenyl]borane, $B(\text{m-XyF})_3$. After crystallization from THF/n-hexane solution, the complex $[\text{WCA-IDipp}](\text{THF})_3$ (6, WCA = $B(\text{m-XyF})_3$) was isolated in moderate yield. (Scheme 3). The $^1$H NMR spectrum (in THF-$d_8$) displays characteristic signals at 6.30 ppm and at 7.55/7.43 ppm for the carbene and $m$-XyF$_3$ CH hydrogen atoms, respectively. The $^{13}$C($^1$H) NMR resonance is found in the expected range at 218.5 ppm. In the $^{11}$B($^1$H) and $^{19}$F($^1$H) NMR spectra, the borate unit gives rise to signals at $-8.71$ and at $-61.9$ ppm, which is in agreement with the values reported for related systems. Crystals suitable for X-ray diffraction analysis could be obtained at room temperature by diffusion of n-hexane into a concentrated THF solution. 6 crystallized in the monoclinic space group $P2_1/n$, and the molecular structure is shown in Figure 6. The obtained bond lengths and angles are in agreement with the already discussed potassium complexes. Again, the WCA-NHC ligand is bound in tilted fashion with a K–C1 bond length of 2.9430(15) Å and additional short contacts in the range 3.264(14)–3.4995(14) Å, involving the ipso- and ortho-carbon atoms of the borate-flanking IDipp substituent. As a result, different K–C–N angles of 106.99(9)$^\circ$ and 150.81(10)$^\circ$ are observed. The potassium coordination sphere is completed by three THF ligands, and the overall geometry around the metal ion is similar to that found for the potassium complex of type VI ($M = K$, Figure 1).

**Conclusions**

Deprotonation of the N-heterocyclic carbene IDipp with n-BuLi in the presence of sodium or potassium bis(trimethylsilyl) amides (NaHMDS/KHMDS) and the reactivity of the intermediate dicarbene species towards fluoroboranes (WCA = $B(\text{C}_6\text{F}_5)_3$, $B(\text{m-XyF})_3$) was studied. While the sodium complex $[\text{WCA-IDipp}](\text{Na}(\text{THF})_3$) (1, WCA = $B(\text{C}_6\text{F}_5)_3$) could be conveniently obtained, the reactivity of the polymeric dicarbene species isolated from the reaction of IDipp with KHMDS/n-BuLi was not unambiguous, but provided evidence for the formation of a mixture of polymeric potassium and lithium-potassium complexes. The latter combination was confirmed crystallographi-
All operations with air- and moisture-sensitive compounds were performed in a glovebox under a dry argon atmosphere (MBraun 2008) or on a vacuum line using Schlenk techniques. All solvents were distilled from Na/benzophenone or Ca$_2$H$_2$O, degassed prior to use and stored over molecular sieves (4 Å). The $^1$H, $^{13}$C($H$), $^1$B($H$), and $^1^1$F($H$) NMR spectra were recorded on Bruker DPX 200 (200 MHz), Bruker AV 300 (300 MHz), Bruker DRX 400 (400 MHz) and Bruker AVIII 600 (600 MHz) devices spectrometers. $^1$H and $^{13}C$($H$) NMR spectra were referenced against the (residual) solvent signals.$^{12}$ Boron trifluoride diethyl etherate (BF$_3$·OEt$_2$) was used as external reference for $^1$B. Trichlorofluoromethane (CFCl$_3$) was used as external reference for $^1^1$F. Chemical shifts are reported in ppm (parts per million). $^1$B($H$), $^{13}$C($H$), and $^{11}$F($H$) NMR spectra were obtained applying composite pulse proton decoupling. Coupling constants ($J$) are reported in Hertz (Hz), and splitting patterns are indicated as $s$ (singlet), $d$ (doublet), $t$ (triplet), q (quartet), m (multiplet), sept (septet) and br (broad). NMR assignments were made using additional 2D NMR experiments and the position of the aryl signals are indicated by $o$ (ortho), $p$ (para), $m$ (meta), and $d$ (distant). Elemental analysis was carried out with a Vario Micro Cube System. Unless otherwise indicated, all starting materials were obtained from Sigma-Aldrich, ABCR, TCI, Acros or Fluka and were purified if necessary. IDipp,$^{26}$ B(C$_6$F$_5$)$_2$,$^{33,36}$ and B(m-XyF)$_2$,$^{33,36}$ were prepared according to literature procedures.

### Experimental Details

$\text{(WCA-IDipp)|Na(THF)}$ (1): IDipp (750 mg, 1.9 mmol, 1 eq) and NaHMDS (353 mg, 1.9 mmol, 1 eq or 1 M in THF, 1.923 mL) were treated with Et$_2$O (30 mL) and THF (0.47 mL, 5.85 mmol, 3 eq) as needed. The suspension was stirred for 10 min and reacted with n-BuLi (1.6 M in n-hexane, 1.21 mL, 1.9 mmol, 1 eq). The suspension darkened and was stirred overnight. The precipitate was filtered off, washed with n-hexane (4·10 mL) and dried under high vacuum. Only 400 out of 600 mg of the isolated precipitate were further reacted and we assumed a connectivity of the type [Na(THF)],IDipp (n = 1; $M = 482.69$ g/mol, 0.82 mmol) and calculated the amount of borane based on that. The precipitate was suspended in toluene (15 mL) and stirred at room temperature. B(C$_6$F$_5$)$_2$ (424 mg, 0.82 mmol) was dissolved in toluene (4 mL) and added dropwise to the stirred solution. The reaction mixture was stirred overnight and the resulting precipitate was filtered off, washed with toluene (3·10 mL) and dried under high vacuum. Crystals suitable for X-ray diffraction analysis were obtained by diffusion of $n$-hexane into a concentrated THF solution. The product 1 was isolated as colorless solid (726 mg, 0.72 mmol, 88%) after recrystallization out of THF/n-hexane. Elemental analysis calc. (%) for $C_{38}H_{66}BF_6Na$: C 59.61, H 5.22, N 2.46; found: C 59.60, H 5.25, N 2.47.

$\text{(WCA-IDipp)|[K(THF)]})$ (4): In a Schlenk flask, IDipp (1.0 g, 2.6 mmol, 1 eq) and HMDS (540 mg, 2.6 mmol, 1 eq) were suspended in diethyl ether (60 mL) and THF (0.63 mL, 7.8 mmol, 3 eq) was added. The reaction mixture became clear and orange. The solution was stirred overnight and the resulting colorless precipitate was filtered off and washed with n-hexane (3·20 mL). After drying under high vacuum the desired product 4 was isolated as a colorless solid (760 mg, 1.8 mmol, 70%). Crystals suitable for X-ray diffraction analysis were obtained by diffusion of n-hexane into a concentrated THF solution of 3. Elemental analysis calc. (%) for $C_{41}H_{76}BF_6K$: C 77.98, H 8.80, N 6.27; found: C 74.35, H 8.57, N 5.82. This values fit with the values calculated for the dicarbanone 7-THF (C$_{49}$H$_{64}$K$_{4}$O$_{4}$): $C = 74.65$, H 8.69, N 5.62), which could not be explained properly. $^1$H NMR (300 MHz, THF-d$_2$): $\delta$ (ppm) = 7.21–6.99 (m, 12 H, aryl-$H$), 6.04 (s, 2 H, CH$_2$-Cl), 3.64–3.58 (m, 4 H, THF), 3.16 (sept, $J_{H,H} = 6.88$ Hz, 4 H, CH$_2$-Cl), 2.97 (sept, $J_{H,H} = 6.84$ Hz, 4 H, CH$_2$-Cl), 1.79–1.75 (m, 4 H, THF), 1.13–0.98 (m, 48 H, CH$_2$-Cl). $C$ (THF-d$_2$) NMR (75 MHz, THF-d$_2$): $\delta$ (ppm) = 146.9 (s, 4 x CN), 140.9 (s, 4 x o-Dipp), 146.6 (s, 4 x o-Dipp), 142.8 (s, 4 x i-Dipp), 129.7 (s, 2 x CH$_2$), 126.7 (s, 2 x CH$_2$), 126.7 (s, 2 x CH$_2$), 125.5 (s, 2 x CH$_2$), 28.2 (s, 4 x CH$_2$-Cl), 26.1 (s, CH$_2$-Cl), 25.6 (s, CH$_2$-Cl), 25.5 (s, 2 x CH$_2$), 25.0 (s, CH$_2$-Cl), 24.9 (s, CH$_2$-Cl), 24.5 (s, CH$_2$-Cl), 24.2 (s, CH$_2$-Cl), 23.8 (s, CH$_2$-Cl).
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