## New Structural Motifs of Lithium N-Heterocyclic Carbene Complexes with Bis(3-tert-butylimidazol-2-ylidene)dialkylborate Ligands<sup>†</sup>

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Employment of bidentate, anionic bis(3-*tert*-butylimidazol-2-ylidene)dialkylborate N-heterocyclic ligands  $[BIM^{tBu}BR_2]^-$  (R = Ph or Me) led to the isolation of two unprecedented lithium carbene complexes: monomeric chelating [(BIM<sup>tBu</sup>BPh<sub>2</sub>)Li(OEt<sub>2</sub>)] (**4a**) and nonchelating, dimeric  $\mu_2$ - $\kappa C^2$ : $\kappa C^2$ -[(BIM<sup>tBu</sup>-BMe<sub>2</sub>)<sub>2</sub>Li<sub>2</sub>] (**4b**). Both have been characterized by spectroscopic methods and by single-crystal X-ray diffraction.

## Introduction

Enormous interest has emerged in the field of N-heterocyclic (NHC) carbene chemistry<sup>1</sup> after Arduengo and co-workers isolated the first stable imidazol-2-ylidene in free form.<sup>2</sup> NHCtype carbenes act as strong  $\sigma$ -donating ligands with the possibility of weak back-bonding capabilities depending on the metal they are bound to (certainly not toward alkali metals) and form stable complexes with a large number of transition metals.<sup>3</sup> In various cases, NHC ligands can serve as useful alternatives to spectator phosphines, and similarities and differences between these two types of ligands are well understood and have been multiply reviewed.<sup>4</sup> The vast majority of studies with NHC ligands, however, focus upon transition metals, while the chemistry of group 1 metals is less explored.<sup>5-14</sup> This is surprising since usually the "free" carbenes may be rather easily generated by deprotonation of the corresponding imidazolium salts with strong group 1 bases, e.g., with KO-t-Bu, NaH, *i*-Pr<sub>2</sub>NLi, or *n*-BuLi, and the knowledge of the structures of primary carbene adducts formed with alkali metals could be important for understanding the mechanism of carbene transfer to transition metals or for NHC reactivity in general.

In 2001, Fehlhammer et al. described the in situ preparation of anionic bis(3-alkylimidazol-2-ylidene)dihydroborates  $[BIM^{Alk}BH_2]$  (Alk = Me, Et, *i*-Pr) as lithium complexes with unspecified structures.<sup>13</sup> These species were successfully applied for the synthesis of Pd(II), Pt(II), and Au(I) NHC complexes. Very recently, Smith et al. reported and structurally characterized lithium carbene complexes with the bulky  $[BIM^{H_0}BH_2]$  ligand and employed them in the preparation of a square-planar nickel(II) tetracarbene complex.<sup>14a</sup> A related, even more recent publication by Hill and co-workers<sup>14b</sup> reported [BIM<sup>1Bu</sup>BH<sub>2</sub>] complexes of the heavier alkaline earths (Ca, Sr), which were investigated by experimental and theoretical (DFT) studies and were shown to be active in intramolecular olefin hydroamination catalysis. This prompted us to develop a novel synthetic approach to still more sterically demanding congeners of the [BIM<sup>Alk</sup>BR<sub>2</sub>] series, since combining their strong binding potential arising from the anionic nature of these ligands with an increased steric bulk was hoped to facilitate structural characterization and to improve the potential catalytic activity of their transition-metal complexes by preventing the decomposition of reactive intermediates.

Herein we report an efficient synthesis of the bidentate, bulky anionic  $[BIM^{Alk}BR_2]^-$  NHC ligands (Alk = *t*-Bu; R = Ph or Me) in the form of their lithium carbene complexes. The molecular structure determination by X-ray diffraction revealed two completely different bonding patterns which to the best of our knowledge do not have precedents in Li NHC chemistry.

The reaction of dialkyl- and diarylboron halides with *N*-tertbutylimidazole (1) proceeded smoothly to afford the corresponding imidazolium salts 2a,b in good to excellent yields (Scheme 1). Treatment of 2 in methanol with ammonium hexafluorophosphate caused complete exchange of bromide or

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 $<sup>^{\</sup>dagger}$  Dedicated to Prof. Werner Tochtermann on the occasion of his 75th birthday.

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chloride counterions and formation of [H2BIMtBuBR2](PF6)2 (3a,b). Different from their chloride or bromide analogues, the imidazolium hexafluorophosphate salts had a high tendency to form crystals and could be characterized by single-crystal X-ray diffraction. The salts **3a** and **3b** can be deprotonated by *n*-BuLi, and subsequent extraction of the organic products with pentane, followed by removal of the solvents in vacuo, afforded the corresponding pure, Li-coordinated carbenes 4a,b as white solids. Deprotonation of 3a with KO-t-Bu has been attempted as well. In this case, however, a complicated mixture of products was obtained, presumably because of a competitive nucleophilic substitution at boron. Alternatively, the free carbenes may also be obtained from the salts 2a,b. Interestingly, 2a was unreactive in this case toward *n*-BuLi, and the carbene 4a could successfully be generated from 2a only with t-BuLi. On the other hand, deprotonation of 2b with n-BuLi proceeded smoothly and gave 4b without incorporation of LiBr.

The structure of **4a** was elucidated by X-ray diffraction analysis. Compound **4a** crystallizes with two independent molecules in the unit cell, and in Figure 1 only one of them is depicted. The molecular structure shows the typical elongation of the  $C_{carbene}$ -N bond distances and a decrease of the

C(21) B N(12) C(11) C(21) B N(12) C(11) N(2) C(1) C(11) N(3) C(1) C(1) C(11)



Figure 2. Structural representations of compounds  $5^8$  and  $5a^{14a}$  reported in the literature.

N-C<sub>carbene</sub>-N angles upon deprotonation of the imidazolium precursor. This is in accordance with the increase of the 2s character of the carbene lone pair.15 At the same time, the  $C_{Ph}$ -B- $C_{Ph}$  angle in **4a** is widened by 5° in comparison to that in salt 3a as a consequence of the chelating binding mode. Lithium carbenes are rare; up to date, there are only a few structurally characterized Li NHC adducts.<sup>5–12,14</sup> Although the average Li- $C_{carbene}$  distance in 4a [2.089(10) Å] is the shortest among them, it deviates by less than 0.1 Å from those found in related solid-state structures. The six-membered chelate ring in 4a has a boat conformation with the Li atom in a trigonal, almost planar environment [the sum of angles around Li is 359°]. This contrasts the dimeric tris(carbene)  $5^8$  (Figure 2) where each Li in the solid state was found in a strongly distorted LiC4tetrahedral arrangement. The bite angle Ccarbene-Li-Ccarbene  $[97.6(4)^{\circ}]$  of **4a** is close to that of the homoleptic complex **5**  $[\alpha = 92.7(2)^{\circ}]$  where both  $C_{carbene}$  atoms belong to the same ligand. The N-B-N angles in 4a [108.5(4)°] and 5 [110.4(2)-111.6(2)°] are also nearly identical. The Li-O separation of 1.964(10) Å is longer than that of 1.893(5) Å found in Arnold's asymmetric lithium alkoxycarbene [LiOCH-t-BuCH<sub>2</sub>(1-C{N-CHCHNMe})]·LiI.<sup>10</sup> Such a difference may be explained in terms of better overall donation from two carbene units in 4a.

To get an idea of how much the observed molecular structure of **4a** is a consequence of the solid state, we have performed DFT calculations<sup>16</sup> for the gas phase for a truncated model, **4a#** (Me<sub>2</sub>O replacing Et<sub>2</sub>O, *N*-*t*-Bu of NHC ring replaced by *N*-Me). The gas-phase [B3LYP/6-31+G(d)] equilibrium structure of **4a#** is presented in Figure 3. As in case of the real molecule in the solid state, the six-membered ring has a boat conformation with *exo-* and *endo-*CH<sub>3</sub> substituents at the boron atom; both carbene carbon atoms, Li, and O lie almost in the same plane. The nitrogen atoms are in a planar environment. The C–N bond lengths are rather short and have partial double bond character, which results from the donation of the nitrogen lone pairs to the vacant carbene orbital. The calculated bond lengths for the model system **4a#** are in good agreement with those in the solidstate structure of **4a**.

In the <sup>1</sup>H NMR spectrum of 4a (in C<sub>6</sub>D<sub>6</sub>) there are three characteristic groups of aromatic signals assignable to *o*-, *m*-,

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**Figure 3.** B3LYP/6-31+G(d)-optimized structure of the model **4a#**. Selected bond lengths (Å) and angles (deg): Li(1)-O(50), 1.951; Li(1)-C(1), 2.076; C(1)-N(2), 1.365; N(2)-B(1), 1.603; N(2)-C(3), 1.385; C(3)-C(4), 1.363; C(4)-N(5), 1.389; N(5)-C(1), 1.369; C-Li-C, 100.81.

and *p*-phenyl protons, indicating either rotation of the NHC moieties around the B-N bonds because of the lability of the Li-C<sub>carbene</sub> bonds or a fast boat-to-boat ring inversion interconverting the two phenyl rings. The imidazole protons appear as two doublets at 7.33 and 6.82 ppm ( ${}^{3}J_{\text{HH}} = 1.5$  Hz). Two broad low-field signals at 199.4 and 156.8 ppm were found in the <sup>13</sup>C NMR spectrum of 4a. Whereas the first resonance is close to that reported for tris(carbene) 5 ( $\delta$  191.0 in CD<sub>3</sub>CN at 65 °C),<sup>8</sup> the second could be attributed to the phenyl carbon attached to the boron atom. The <sup>13</sup>C NMR spectrum of 4a in THF- $d_8$ displays a rather sharp and perfectly visible carbene resonance at 202.9 ppm. In this case, substitution of the Et<sub>2</sub>O ligand by the more strongly coordinating THF- $d_8$  should be feasible. The shape of these low-field signals generally depends strongly on the choice of the solvent and the temperature (see the Supporting Information).

Deprotonation of **3b** under the same reaction conditions as for compound **3a** afforded the lithium carbene **4b** without coordinated solvent, as was established by <sup>1</sup>H NMR spectroscopy. Crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated solution of **4b** in pentane.

In the solid state (Figure 4), both lithium atoms and four carbene carbons of a dimeric molecule share the same plane. Each lithium atom is coordinated by two carbene carbons of different bis(carbene) ligands in a  $\mu_2$ - $\kappa C^2$ : $\kappa C^2$ ' manner. Both endo-methyl groups of the two BMe2 fragments show CH interactions with both lithium atoms in a  $\mu$ -fashion, with a planar arrangement of the [Li<sub>2</sub>H<sub>2</sub>] core, and we note that in Hill's Ca and Sr complexes with [BIM<sup>tBu</sup>BH<sub>2</sub>]<sup>-</sup> ligands a boron-bound hydrogen displays an "agostic-type" interaction, which actually was analyzed as mainly electrostatic in nature. The phenomenon of CH interactions with the Li centers in 4b is reflected in the C(22)-H(22c) bond lengths elongated by ca. 0.04 Å and B-C(22)-H(22c) angles increased by ca. 8° as compared to the two methyl groups pointing away from the Li-Li core. The solid-state structure of 4b overall is considerably different from that of dimeric carbene 5a (Figure 2) where both two- and threecoordinate lithium atoms have been found.<sup>14a</sup>

The  $[Li_2H_2]$  moiety looks similar to the  $[Li_2N_2]$  core of Arnold's amido-tethered dimeric lithium carbene complex with a *tert*-butyl-[2-(3-*tert*-butylimidazol-2-ylidene)ethyl]amide ligand.<sup>12</sup> The nonlinear C<sub>carbene</sub>-Li-C<sub>carbene</sub> angles of 160.0(3)° and 168.2(3)° must be a consequence of these Li<sub>2</sub>-CH<sub>3</sub> interactions as well. The observed Li-H contacts (average



Figure 4. ORTEP plot of 4b at 40% probability ellipsoids. Some hydrogen atoms are omitted.

2.12(2) Å) may be in part responsible for the "trans" position of the BMe<sub>2</sub> tethers, i.e., their position at opposite sides of the [Li<sub>2</sub>C<sub>4</sub>] plane. It is worth noting that, in the solid-state structures of the nonchelating, cationic bis(carbene) silver(I) or gold(I) complexes [(BIM<sup>Alk</sup>)<sub>2</sub>Ag<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (Alk = n-Bu<sup>17</sup> or Mes<sup>18</sup>) and [(BIM<sup>Me</sup>)<sub>2</sub>Au<sub>2</sub>]I<sub>2</sub><sup>19</sup> [BIM = bis(3-*tert*-butylimidazol-2-ylidene)methane] two CH<sub>2</sub> tethers of the ligands are "cis" to each other; i.e., they protrude in the same direction from the metal core. A similar picture is also observed in the solid-state structure of [(BIM<sup>Et</sup>BH<sub>2</sub>)<sub>2</sub>Au<sub>2</sub>].<sup>13</sup>

The average Li–C<sub>carbene</sub> distance in **4b** of 2.056(2) Å is even shorter than that found for its monochelating analogue **4a**. This value may be compared with the longest C<sub>carbene</sub>–H distance [2.026 Å] in the cationic bis(carbene)–proton complex [NHC–H<sup>+</sup>–NHC]X<sup>-</sup> [NHC =:C(MesNCHCHNMes), X = PF<sub>6</sub> or CF<sub>3</sub>SO<sub>3</sub>] isolated by Arduengo et al.<sup>20</sup>

Complexes **4a,b** represent novel structural patterns; to the best of our knowledge there are no lithium carbenes with ML<sub>3</sub> or  $\mu_2$ - $\kappa C^2$ : $\kappa C^2$ ' bonding motifs which have been structurally characterized previously. The relatively small methyl groups at the boron atom allow the formation of the dimeric species **4b**, whereas in the case of chelate **4a** the two large phenyl groups preclude the aggregation of the monomers.

NMR spectra of dimer **4b** in  $C_6D_6$  showed broad peaks, presumably due to fluxional exchange processes and were thus not informative. In the <sup>1</sup>H NMR spectra of **4b** recorded in THF- $d_8$ , the methyl groups at the boron atoms give rise to one rather broad singlet at 0.18 ppm, while the imidazole protons display resonances at 6.93 and 6.81 ppm with a small coupling constant of  ${}^{3}J_{\text{HH}} = 1.4$  Hz. Most probably, in strongly coordinating solvents such as THF compound **4b** exists as a solvated chelate similar to the ether adduct **4a**. Indeed, deprotonation of the imidazolium salt **2b** or **3b** with *n*-BuLi using THF as a solvent, followed by extraction with pentane, afforded a ca. 1:1 complex, **4b** • THF, with spectroscopic properties (in THF- $d_8$ ) identical to those of **4b**. The carbene carbon signal of both samples

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appears at 198.7 ppm (THF- $d_8$ ). Carbenes **4a**,**b** and **4b** · THF are stable in the solid state or in solution at room temperature, but they are extremely sensitive to air.

In conclusion, we describe here a convenient method for the synthesis of sterically demanding anionic ligands [BIM<sup>tBu</sup>BR<sub>2</sub>] (R = Ph or Me) which enabled us to structurally characterize two unprecedented, chelating ML<sub>3</sub>-type and nonchelating  $\mu_{2}$ - $\kappa C^2$ : $\kappa C^2$ '-type lithium carbene complexes with strikingly different bonding motifs in the solid state. The results presented in this work add to understanding the properties and composition of lithium carbene adducts **4a**,**b** are promising reagents for carbene transfer reactions which are under way in our laboratory and will be reported in due course.

## **Experimental Section**

Unless otherwise stated, all the experiments were performed under an Ar atmosphere using a Braun glovebox or by Schlenk techniques. THF, pentane, and diethyl ether were distilled over benzophenone sodium ketyl and kept under Ar. Benzene- $d_6$  and DMSO- $d_6$  were stirred over CaH<sub>2</sub> and then degassed three times prior to use. THF- $d_8$  was distilled over sodium and also degassed three times. *N-tert*-Butylimidazole,<sup>21</sup> Ph<sub>2</sub>BCl,<sup>22</sup> and Me<sub>2</sub>BBr<sup>23</sup> were prepared according to known procedures. NMR spectra were recorded on a Bruker 500, 300, or 250 MHz spectrometer at the temperatures specified below. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in parts per million and are referenced to the deuterated solvents used.

[H<sub>2</sub>BIM<sup>tBu</sup>BPh<sub>2</sub>]Cl (2a). To a solution of *N*-tert-butylimidazole (6.1 g, 49.2 mmol) in absolute toluene (25 mL) at 0 °C was added slowly a solution of Ph<sub>2</sub>BCl (3.79 g, 18.9 mmol) in absolute toluene (25 mL), and a white precipitate started to form after 1 min. The reaction mixture was stirred at room temperature (rt) for 15 min and then at 110 °C for 48 h. The white suspension was filtered under Ar, and the white precipitate obtained was washed with dry toluene (5  $\times$  10 mL) and dry hexane (5  $\times$  10 mL) and was dried at  $10^{-3}$  mbar to give a white light powder, 7.60 g (89.5%), mp 227-228 °C. The product is only slightly soluble in THF, Et<sub>2</sub>O, and toluene, but easily soluble in DMSO or MeOH. <sup>1</sup>H NMR (300.13 MHz, DMSO- $d_6$ , 305 K): 8.38 (pseudo-t, 2H,  ${}^{3}J_{HH} = 1.6$ Hz, 2H imidazole), 7.94 (pseudo-t, 2H,  ${}^{3}J_{HH} = 1.7$  Hz, 2H imidazole), 7.23–7.32 (m, 6 aromatic H), 7.21 (pseudo-t, 2H,  ${}^{3}J_{HH}$ = 1.6 Hz, 2H imidazole), 7.06–7.10 (m, 4 aromatic H), 1.57 (s, 18H, NC(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.48 MHz, DMSO-*d*<sub>6</sub>, 305 K): 135.7 (s, imidazole C), 132.9 (s, aromatic C), 127.4 (s, aromatic C), 126.6 (s, aromatic C), 125.0 (s, imidazole C), 119.9 (s, imidazole C), 58.3 (s, NC(CH<sub>3</sub>)<sub>3</sub>), 29.0 (s, NC(CH<sub>3</sub>)<sub>3</sub>). MS-ESI: m/z (rel intens, %) 413.4 (M - Cl)<sup>+</sup> (25). Anal. Calcd for C<sub>26</sub>H<sub>34</sub>BClN<sub>4</sub>: C, 69.58; H, 7.64; N, 12.48. Found: C, 68.81; H, 7.61; N, 12.22.

[H<sub>2</sub>BIM<sup>tBu</sup>BMe<sub>2</sub>]Br (2b). To a solution of *N-tert*-butylimidazole (11.98 g, 96.6 mmol) in absolute toluene (160 mL) was added dropwise at -20 °C a solution of Me<sub>2</sub>BBr (5.37 g, 44.4 mmol) in absolute toluene (20 mL). The reaction mixture was allowed to warm to rt and then was refluxed for 4 h. The white suspension was filtered, washed three times with toluene and three times with pentane, and dried at  $10^{-3}$  mbar to yield 15.4 g (94%) of a white, very fine powder, mp 225–227 °C dec. Compound **2b** turned out to be neither hygroscopic nor air-sensitive. <sup>1</sup>H NMR (500.13 MHz,

DMSO-*d*<sub>6</sub>, 298 K): 8.57 (br s, 2H imidazole), 7.78 (br s, 2H imidazole), 7.37 (br s, 2H imidazole), 1.56 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.26 (s, 6H, B(CH<sub>3</sub>)<sub>2</sub>).  ${}^{13}C{}^{1}H$  NMR (125.77 MHz, DMSO-*d*<sub>6</sub>, 298 K): 133.9, 123.0, 119.8 (all s, imidazole C), 57.9 (s, C(CH<sub>3</sub>)<sub>3</sub>), 29.3 (s, C(CH<sub>3</sub>)<sub>3</sub>), 8.47 (br s, B(CH<sub>3</sub>)<sub>2</sub>). MS-ESI: *m*/*z* (rel intens, %) 145 (100) [(M - 2(*t*-Bu) - 2Me - Br)<sup>+</sup>], 289 (90) [(M - Br)<sup>+</sup>].

[H<sub>2</sub>BIM<sup>tBu</sup>BPh<sub>2</sub>]PF<sub>6</sub> (3a). The experiment was performed under air. To a solution of the chloride 2a (3 g, 6.7 mmol) in MeOH (100 mL) was added in several portions well-milled NH<sub>4</sub>PF<sub>6</sub> (3.27 g, 20.1 mmol). The reaction mixture was stirred at rt for several hours, the solids were filtered off and washed on the filter with MeOH, and the methanol washings were discarded. The remaining solid was thoroughly washed with CH<sub>2</sub>Cl<sub>2</sub>, and the filtrate was evaporated (the desired salt is very soluble in CH2Cl2, unlike NH<sub>4</sub>PF<sub>6</sub> and NH<sub>4</sub>Br). The residue obtained was recrystallized from  $CH_2Cl_2$  – MeOH to afford a white microcrystalline solid (2.85 g, 75%), mp 213-214 °C. Samples of 3a suitable for X-ray analysis were obtained by slow crystallization from the diluted methanol solution at room temperature. <sup>1</sup>H NMR (500.13 MHz, DMSO-d<sub>6</sub>, 298 K): 8.36 (s, 2H imidazole), 7.90 (s, 2H imidazole), 7.22-7.29 (m, 8H, 2H imidazole + 6H aromatic), 7.06-7.08 (m, 4 aromatic H). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, DMSO-*d*<sub>6</sub>, 298 K): 135.7, 133.0, 127.5, 126.7, 125.1, 119.9 (all aromatic and imidazole C), 58.4 (s,  $NC(CH_3)_3$ , 29.1 (s,  $NC(CH_3)_3$ ). Anal. Calcd for  $C_{26}H_{34}BF_6N_4P$ : C, 55.93; H, 6.14; N, 10.03; P, 5.55. Found: C, 55.81; H, 6.12; N, 10.03; P, 5.51.

[H<sub>2</sub>BIM<sup>tBu</sup>BMe<sub>2</sub>]PF<sub>6</sub> (3b). The synthesis was carried out under air. To a stirred solution of bromide 2b (2.0 g, 5.42 mmol) in MeOH (150 mL) was added portionwise well-milled NH<sub>4</sub>PF<sub>6</sub> (1.943 g, 11.92 mmol). The reaction mixture was stirred for 4 h and filtered. The solid on the filter was washed with MeOH (20 mL), the methanol fractions were combined, and the solvent was completely removed. The solid residue was treated with CH2Cl2 (120 mL) and filtered. The residual solid (presumably a mixture of NH<sub>4</sub>Br and  $NH_4PF_6$ ) was washed with  $CH_2Cl_2$  (30 mL), and the combined dichloromethane solutions were evaporated. The solid obtained was dissolved in a minimum amount of hot methanol (30-40 mL), and the solution was slowly cooled to -20 °C and kept at this temperature overnight. The separated crystals were collected on a filter, washed with Et<sub>2</sub>O, and then dried in vacuo to yield 1.333 g (57%) of crystalline product, mp 149-151 °C. <sup>1</sup>H NMR (500.13 MHz, DMSO-d<sub>6</sub>, 298 K): 8.47 (pseudo-t, 2H imidazole), 7.76 (pseudo-t, 2H imidazole), 7.34 (pseudo-t, 2H imidazole), 1.56 (s + sat,  ${}^{1}J_{CH} = 127.6$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.26 (s + sat,  ${}^{1}J_{CH} = 114.5$ Hz, 6H, B(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, DMSO-d<sub>6</sub>, 298 K): 133.8, 123.1, 119.9 (all s, imidazole C), 58.0 (s, C(CH<sub>3</sub>)<sub>3</sub>), 29.3 (s, C(CH<sub>3</sub>)<sub>3</sub>), 8.49 (br s, B(CH<sub>3</sub>)<sub>2</sub>). MS-ESI: *m*/*z* (rel intens, %)  $125.6 (40) [(C_7H_{12}N_2 + H)^+], 289.6 (20) [(M - PF_6)^+].$  Anal. Calcd for C<sub>16</sub>H<sub>30</sub>BF<sub>6</sub>N<sub>4</sub>P: C, 44.26; H, 6.96; N, 12.90; P, 7.13. Found: C, 44.12; H, 6.95; N, 12.72; P, 7.18.

[Li(BIM<sup>iBu</sup>BPh<sub>2</sub>) · Et<sub>2</sub>O] (4a). To a suspension of the salt 3a (0.3 g, 0.54 mmol) in Et<sub>2</sub>O (10 mL) was added at -70 °C a solution of n-BuLi (1.096 mmol) in hexane (0.62 mL). The reaction mixture was allowed to warm to ambient temperature and then was stirred for 3 h to form a clear solution. The solvent was removed at  $10^{-3}$ mbar, and the residue was extracted with absolute pentane  $(2 \times 10)$ mL) and evaporated to give 70 mg of the carbene 4a as a white powder. Crystals of 4a suitable for X-ray analysis were obtained by slow evaporation of its freshly prepared pentane solution. <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): 7.58 (d,  ${}^{3}J_{HH} = 7.2$  Hz, 4H ortho-aromatic), 7.40 (pseudo-t,  ${}^{3}J_{HH} = 7.7$  Hz, 4H meta-aromatic), 7.34 (d,  ${}^{3}J_{\text{HH}} = 1.5$  Hz, 2H imidazole), 7.32 (pseudo-t,  ${}^{3}J_{\text{HH}} = 7.5$ Hz, 2H para-aromatic), 6.81 (d,  ${}^{3}J_{HH} = 1.5$  Hz, 2H imidazole), 3.03 (q,  ${}^{3}J_{\text{HH}} = 7.2$  Hz, 4H, 2OCH<sub>2</sub>), 1.43 (s, 18H, NC(CH<sub>3</sub>)<sub>3</sub>), 0.88 (t,  ${}^{3}J_{\text{HH}} = 7.2$  Hz, 6H, CH<sub>3</sub>).  ${}^{13}C{}^{1}H{}$  NMR (125.77 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): 199.4 (br s, C<sub>carbene</sub>), 156.8 (br s), 135.4, 127.0, 126.6,

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125.4, 112.4 (s, aromatic + imidazole C), 64.8 (s, OCH<sub>2</sub>), 54.5 (s, NC(CH<sub>3</sub>)<sub>3</sub>), 31.5 (s, NC(CH<sub>3</sub>)<sub>3</sub>), 14.4 (s, CH<sub>3</sub>).

[Li<sub>2</sub>(BIM<sup>tBu</sup>BMe<sub>2</sub>)<sub>2</sub>] (4b). To a stirred suspension of the salt 3b (0.5 g, 1.15 mmol) in Et<sub>2</sub>O (8 mL) was added dropwise at  $-78 \text{ }^{\circ}\text{C}$ a solution of *n*-BuLi (2.02 equiv, 2.32 mmol) in hexane (1.31 mL). The reaction mixture was allowed to warm to rt and then was stirred at rt for 3.5 h until all of the crystalline salt had dissolved. The solvent was removed at 10<sup>-3</sup> mbar, and the residue was treated with pentane (15 mL) under vigorous stirring. The white sticky solid was allowed to precipitate, and the clear solution was filtered via a filter cannula into a separate Schlenk vessel. The extraction was repeated with additional pentane (10 mL). The combined pentane solutions were evaporated at  $10^{-3}$  mbar and dried at the same vacuum to yield 220 mg (65%) of a white powder. Alternatively, the nonsolvated carbene 4b can be generated from the bromide salt 2b. In this case, however, some unidentified side products were detected by <sup>1</sup>H NMR spectroscopy. Crystals of 4b suitable for X-ray analysis were obtained from its freshly prepared concentrated pentane solution upon standing at room temperature. <sup>1</sup>H NMR (300.13 MHz, THF- $d_8$ , 298 K): 6.93 (d, <sup>3</sup> $J_{HH} = 1.2$  Hz, 2H imidazole), 6.81 (d,  ${}^{3}J_{HH} = 1.2$  Hz, 2H imidazole), 1.50 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.18 (s, 6H, B(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.47 MHz, THF-d<sub>8</sub>, 298 K): 198.8 (s, C<sub>carbene</sub>), 121.5, 112.5 (all s, imidazole C), 54.9 (s, C(CH<sub>3</sub>)<sub>3</sub>), 31.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 13.8 (br s, B(CH<sub>3</sub>)<sub>2</sub>).

[Li(BIM<sup>tBu</sup>BMe<sub>2</sub>) · THF] (4b · THF). To a stirred suspension of the imidazolium salt 2b (400 mg, 1.08 mmol) in absolute THF (8 mL) was added dropwise at -78 °C a solution of n-BuLi in hexane (1.24 mL, 2.2 mmol). The cooling bath was removed, and the reaction mixture was allowed to warm to rt. Upon warming, the solid started to dissolve, so that after stirring at ambient temperature for ca. 30 min, a clear, slightly yellow solution was obtained. The solvent was removed in vacuo at  $10^{-3}$  mbar, and the foamlike material obtained was treated with pentane (20 mL) and vigorously stirred. The solid (LiBr) was allowed to precipitate, and the clear solution above it was decanted via a filter cannula. The extraction procedure was repeated again with 10 mL of pentane, and the combined pentane solutions were evaporated at  $10^{-3}$  mbar. The white foam obtained was crushed to a powder and dried at  $10^{-3}$ mbar. Yield: 235 mg (59.3%). <sup>1</sup>H NMR (500.13 MHz, THF-d<sub>8</sub>, 298 K): 6.93 (d,  ${}^{3}J_{HH} = 1.4$  Hz, 2H imidazole), 6.81 (d,  ${}^{3}J_{HH} = 1.4$ Hz, 2H imidazole), 3.60-3.65 (m, ca. 4H, THF), 1.76-1.80 (m, ca. 4H, THF), 1.51 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.18 (s, 6H, B(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, THF-*d*<sub>8</sub>, 298 K): 198.7 (s, C<sub>carbene</sub>), 121.5, 112.5 (all s, imidazole C), 68.1 (s, THF), 54.9 (s, *C*(CH<sub>3</sub>)<sub>3</sub>), 31.8 (s, *C*(*C*H<sub>3</sub>)<sub>3</sub>), 26.3 (s, THF), 13.7 (br s, B(*C*H<sub>3</sub>)<sub>2</sub>).

**Crystal Structure Analysis.** Data were collected on SMART CCD diffractometers, and the structure solutions were obtained using the SHELXTL-PLUS (5.10) software package.<sup>24</sup> Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS<sup>25</sup> based on the Laue symmetry of the reciprocal space.

**Crystallographic Data for 4a.**  $C_{30}H_{42}BLiN_4O$ , M = 492.43, crystal system monoclinic, space group  $P_{21}/c$ , Z = 8, a = 18.5920(8) Å, b = 16.6504(7) Å, c = 19.6531(9) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 93.190(1)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 6074.5(5) Å<sup>3</sup>, T = 200(2) K,  $\theta_{max} = 19.8^{\circ}$ , radiation Mo K $\alpha$ ,  $\lambda = 0.71073$  Å, 30 297 reflections measured, 5508 unique ( $R_{int} = 0.1031$ ), 3186 observed ( $I > 2\sigma(I)$ ), final residual values R1(F) = 0.059, wR(F2) = 0.132 for observed reflections.

**Crystallographic Data for 4b.**  $C_{34.50}H_{62}B_2Li_2N_8$ , M = 624.42, crystal system tetragonal, space group  $P4_2/n$ , Z = 4, a = 12.0986(1) Å, b = 12.0986(1) Å, c = 26.0609(1) Å,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ , V = 3814.69(5) Å<sup>3</sup>, T = 200(2) K,  $\theta_{max} = 24.6^\circ$ , 31 499 reflections measured, 3231 unique (R(int) = 0.0554), 2102 observed ( $I > 2\sigma(I)$ ), final residual values R1(F) = 0.042, wR(F2) = 0.102 for observed reflections.

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Supporting Information Available: Crystallographic data and ORTEP plots of **3a,b**, further experimental, spectroscopic, and/or structural details for compounds 2-4 and  $4b \cdot \text{THF}$ , and atomic coordinates for the B3LYP/6-31+G(d)-optimized model **4a#**. This material is available free of charge via the Internet at http://pubs.acs.org.

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