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Solid-State and Electronic Structure of Benzoxazol-2-ylidene−triphenylborane Complex

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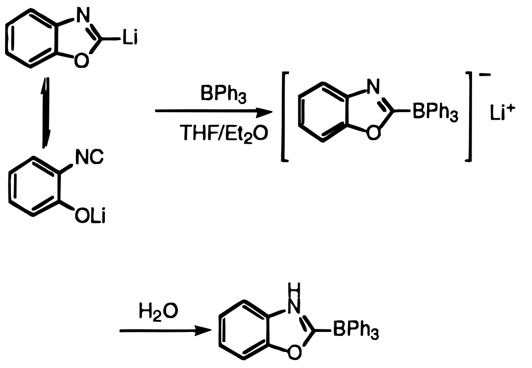
Summary: The X-ray structure of the title compound (synthesized by the reaction of 2-lithiobenzoxazole with triphenylborane and subsequent hydrolysis with water) reveals in comparison with the MP2(FC)/6-31G optimized structures of the model compound oxazol-2-ylidene-borane complex, the free oxazol-2-ylidene carbene, and the oxazolium cation that the borane complex is a true main-group metal carbene complex of the Fischer type and that it tends to be more similar to the free carbene than to the oxazolium cation.*

Introduction

Since the recent discovery of *stable* imidazol-2-ylidene carbenes by Arduengo et al.[1] the chemistry of nucleophilic carbenes has attracted considerable attention which subsequently has led to the synthesis and characterization of a number of main-group Lewis acid adducts of these carbenes.[2] Isoelectronic carbenes such as oxazol-2-ylidene, thiazol-2-ylidene, or their benzannelated derivatives have not been isolated so far due to their instability.[3,4] Many transition metal complexes of these carbenes are known with a wide variety of metals;[5] however, no structural characterization of a main-group analogue has been published until now. In the following we report on the synthesis and the solid-state structure of benzoxazol-2-ylidene−triphenylborane (**1**), which can be conceived as a complex of benzoxazol-2-ylidene carbene and the Lewis acid triphenylborane.

Results and Discussion

While complexes of imidazol-2-ylidene derivatives with Lewis acids have been prepared by direct reaction of the free carbene with the Lewis acid,[2] this route seems not to be feasible for synthesizing complexes of benzoxazol-2-ylidene because of its instability. Hence, we chose a different way similar to the preparation of transition metal carbene complexes of thiazoles by Raubenheimer et al.:[5d] lithiation of benzoxazole in THF/ether solution leads to an equilibrium of 2-lithiobenzoxazole and lithium 2-isocyanophenoxide (see eq 1).[6]



(1)

1

However, reaction with the soft Lewis acid triphenylborane yielded pure lithium benzoxazol-2-yl−triphenyl borate. Subsequent hydrolysis with water gave **1** in moderate yield as the only isolable product. Complex **1**, which could be characterized by X-ray crystallography (see Figure 1, Tables 1−3), is remarkably stable toward air and moisture over several months.

All four C−B contacts in **1** lie within 1.629−1.648 Å; the C−B−C angles also show only small deviations: 106.4−114.4°. Hence, **1** has an almost undistorted tetrahedral geometry around boron, similar to the BPh_4^- anion, although the latter has somewhat longer C−B bonds (1.64−1.69 Å).[7] Comparison of the bonding

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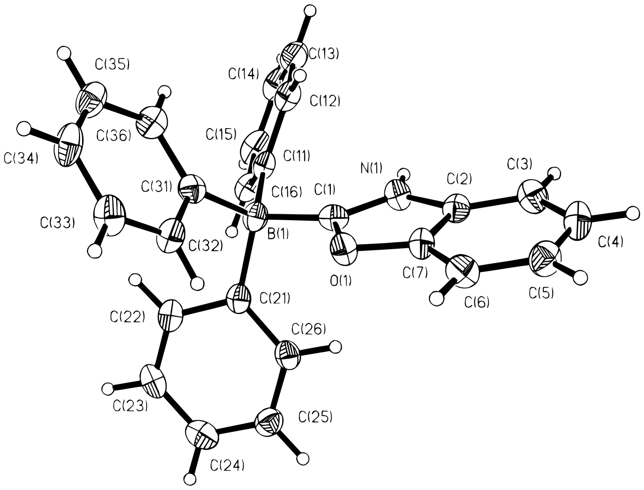
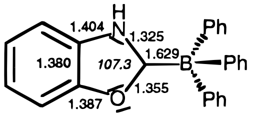


Figure 1. X-ray structure of **1** showing 50% thermal ellipsoids.



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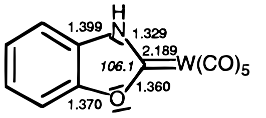

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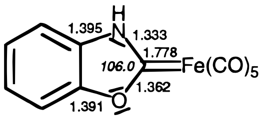

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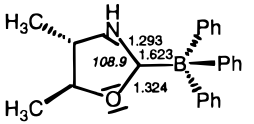

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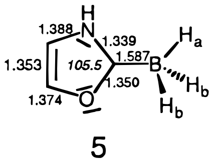

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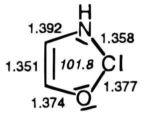

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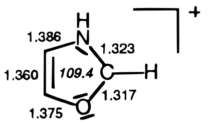

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parameters (Table 3) of the benzoxazol-2-ylidene fragment in **1** with those of the recently published X-ray structures of benzoxazol-2-ylidene−tungstenpentacarbonyl (**2**)[5a] and of benzoxazol-2-ylidene−irontetracarbonyl (**3**)[5e] shows that the substitution of the $W(CO)_5$ or the $Fe(CO)_4$ fragment of BPh_3 does not change the organic rest at all. Especially the C2−N and C2−O bonds are very similar in all three structures. Thus, from a structural point of view, **1** can be conceived as a true main-group carbene complex of Fischer type. The C2−B bond in **1** (1.629 Å) is very simlar to that of an already known solid-state structure of (*trans*-4,5-dimethyloxazolidin-2-ylidene)triphenylborane (**4**; 1.623 Å),[8] whereas the C2−N and C2−O bonds in **1** are significantly longer than those in **4** due to increased π delocalization in the five-membered ring in the former compound.[5e] To our knowledge, the only other known triorganboron adduct with a carbon Lewis acid is that of a substituted cyclopropenylidene carbene with BAr_3 (C−B distance 1.623 Å).[9]

Table 1. Crystal Data and Structure Refinement for 1

formula	$C_{25}H_{20}BNO$
formula weight	361.23
crystal system	triclinic
space group	$P\bar{1}$
a (Å)	9.586(2)
b (Å)	9.978(2)
c (Å)	10.777(2)
α (deg)	80.51(3)
β (deg)	79.91(3)
γ (deg)	73.49(3)
V (Å^3)	965.8(3)
Z	2
density (calc) (Mg/m^3)	1.242
θ (deg)	3.61−22.50
no. of reflections collected	4376
no. of Independent reflections	2520
data/restraints/parameters	2517/0/253
GOF	0.976
R1, wR2 ($I > 2\sigma(I)$)	0.0446/0.0903
largest diff peak and hole (eÅ^{-3})	0.148 and −0.185

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times 10^3$) for 1[a]

	x	y	z	U(eq)
B(1)	1767(4)	6157(3)	7889(3)	26(1)
O(1)	1631(2)	8013(2)	9386(2)	28(1)
N(1)	2049(2)	5897(2)	10362(2)	27(1)
C(1)	1842(3)	6643(3)	9241(3)	26(1)
C(2)	1982(3)	6757(3)	11291(3)	25(1)
C(3)	2100(3)	6520(3)	12572(3)	32(1)
C(4)	1933(3)	7700(3)	13159(3)	35(1)
C(5)	1652(3)	9056(3)	12495(3)	33(1)
C(6)	1536(3)	9284(3)	11209(3)	31(1)
C(7)	1709(3)	8098(3)	10642(2)	25(1)
C(11)	2400(3)	4446(3)	8012(2)	26(1)
C(12)	3780(3)	3754(3)	8388(3)	32(1)
C(13)	4332(4)	2294(3)	8494(3)	39(1)
C(14)	3511(4)	1468(3)	8216(3)	41(1)
C(15)	2156(4)	2112(3)	7827(3)	39(1)
C(16)	1616(3)	3570(3)	7726(3)	30(1)
C(21)	51(3)	6669(3)	7653(2)	25(1)
C(22)	−302(3)	6676(3)	6441(3)	31(1)
C(23)	−1728(3)	7082(3)	6159(3)	33(1)
C(24)	−2887(3)	7542(3)	7088(3)	37(1)
C(25)	−2595(3)	7556(3)	8294(3)	31(1)
C(26)	−1155(3)	7116(3)	8572(3)	27(1)
C(31)	2731(3)	7016(3)	6794(3)	26(1)
C(32)	2223(3)	8479(3)	6515(3)	31(1)
C(33)	2967(4)	9253(3)	5579(3)	35(1)
C(34)	4248(4)	8581(3)	4870(3)	35(1)
C(35)	4768(3)	7146(3)	5108(3)	33(1)
C(36)	4030(3)	6373(3)	6063(3)	30(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

In contrast to **4**, we could observe a broad carbene C2 signal in the ^{13}C-NMR spectrum at 197.5 ppm; however, no coupling pattern was visible probably owing to the quadrupole relaxation of the ^{10}B and ^{11}B nuclei.

How does BPh_3 complexation change the geometry and the electronic structure of the free benzoxazol-2-ylidene carbene? To answer this question we performed *ab initio* computations at MP2(FC)/6-31G*//MP2(FC)/6-31G* level[10] on the model compound oxazol-2-ylidene−borane (**5**), the free oxazol-2-ylidene carbene (**6**),[11] and the protonated carbene (oxazolium cation) **7**. In view of the crudeness of the model the bond distances in the five-membered ring of **5** are in reasonably good agreement with those of **1**. The C−B bond (1.587 Å) in **5** is

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Table 3. Bond Lengths (Å) and Angles (deg) for 1

Bond Lengths			
B(1)−C(21)	1.630(4)	B(1)−C(1)	1.629(4)
B(1)−C(11)	1.632(4)	B(1)−C(31)	1.648(4)
O(1)−C(1)	1.355(3)	O(1)−C(7)	1.387(3)
N(1)−C(1)	1.325(3)	N(1)−C(2)	1.404(3)
C(2)−C(3)	1.381(4)	C(2)−C(7)	1.380(4)
C(3)−C(4)	1.384(4)	C(4)−C(5)	1.399(4)
C(5)−C(6)	1.386(4)	C(6)−C(7)	1.375(4)
C(11)−C(12)	1.403(4)	C(11)−C(16)	1.403(4)
C(12)−C(13)	1.394(4)	C(13)−C(14)	1.386(4)
C(14)−C(15)	1.380(5)	C(15)−C(16)	1.391(4)
C(21)−C(26)	1.402(4)	C(21)−C(22)	1.405(4)
C(22)−C(23)	1.384(4)	C(23)−C(24)	1.386(4)
C(24)−C(25)	1.379(4)	C(25)−C(26)	1.395(4)
C(31)−C(36)	1.397(4)	C(31)−C(32)	1.400(4)
C(32)−C(33)	1.388(4)	C(33)−C(34)	1.383(4)
C(34)−C(35)	1.372(4)	C(35)−C(36)	1.396(4)
Bond Angles			
C(21)−B(1)−C(1)	107.0(2)	C(21)−B(1)−C(11)	112.1(2)
C(1)−B(1)−C(11)	107.2(2)	C(21)−B(1)−C(31)	109.2(2)
C(1)−B(1)−C(31)	106.4(2)	C(11)−B(1)−C(31)	114.4(2)
C(1)−O(1)−C(7)	108.5(2)	C(1)−N(1)−C(2)	111.8(2)
N(1)−C(1)−O(1)	107.3(2)	N(1)−C(1)−B(1)	130.8(2)
O(1)−C(1)−B(1)	121.9(2)	C(3)−C(2)−C(7)	121.5(3)
C(3)−C(2)−N(1)	134.7(2)	C(7)−C(2)−N(1)	103.7(2)
C(2)−C(3)−C(4)	116.2(3)	C(3)−C(4)−C(5)	121.9(3)
C(6)−C(5)−C(4)	121.5(3)	C(7)−C(6)−C(5)	115.7(3)
C(6)−C(7)−C(2)	123.2(3)	C(6)−C(7)−O(1)	128.1(2)
C(2)−C(7)−O(1)	108.7(2)	C(12)−C(11)−C(16)	115.4(3)
C(12)−C(11)−B(1)	122.2(2)	C(16)−C(11)−B(1)	122.4(3)
C(13)−C(12)−C(11)	122.7(3)	C(14)−C(13)−C(12)	119.9(3)
C(15)−C(14)−C(13)	119.1(3)	C(14)−C(15)−C(16)	120.4(3)
C(15)−C(16)−C(11)	112.5(3)	C(26)−C(21)−C(22)	115.1(3)
C(26)−C(21)−B(1)	125.7(2)	C(22)−C(21)−B(1)	119.3(2)
C(23)−C(22)−C(21)	123.1(3)	C(22)−C(23)−C(24)	120.0(3)
C(25)−C(24)−C(23)	118.9(3)	C(24)−C(25)−C(26)	120.5(3)
C(25)−C(26)−C(21)	122.3(3)	C(36)−C(31)−C(32)	116.0(2)
C(36)−C(31)−B(1)	124.2(2)	C(32)−C(31)−B(1)	119.8(2)
C(33)−C(32)−C(31)	122.4(3)	C(34)−C(33)−C(32)	120.1(3)
C(35)−C(34)−C(33)	119.0(3)	C(34)−C(35)−C(36)	120.7(3)
C(35)−C(36)−C(31)	121.8(3)		

Table 4. Calculated Bond Parameters, Wiberg Bond Indices, π NBO Electron Densities, and Total NBO Charges of 5, 6, and 7 at MP2(FC)/6-31G*//MP2(FC)/6-31G* Level

	6	Δ[a]	**5**	Δ[a]	**7**
distances (Å)					
C2−O	1.377	−0.027	1.350	−0.033	1.317
C2−N	1.358	−0.019	1.339	−0.016	1.323
O−C5	1.374	0	1.474	0.001	1.375
C4−C5	1.351	0.002	1.353	0.007	1.360
N−C4	1.392	−0.004	1.388	−0.002	1.386
angles (deg)					
N−C2−O	101.8	3.7	105.5	3.9	109.4
C2−N−C4	114.2	−2.3	111.9	−2.7	109.2
N−C4−C5	104.0	0.4	104.4	0.7	105.1
C4−C5−O	108.5	0.2	108.7	−0.3	108.4
C5−O−C2	111.6	−2.1	109.5	−1.6	107.9
Wiberg bond indices					
C2−O	1.016	0.056	1.072	0.094	1.166
C2−N	1.266	0.049	1.315	0.105	1.420
O−C5	0.970	−0.008	0.962	−0.005	0.957
C4−C5	1.794	0.002	1.796	0.036	1.760
N−C4	1.053	0.006	1.059	0.015	1.074
π electron density					
C2	0.463	0.127	0.590	0.140	0.730
O	1.760	−0.007	1.753	−0.047	1.706
N	1.660	−0.040	1.620	−0.081	1.539
C4	1.081	−0.011	1.070	0.026	1.044
C5	1.037	−0.001	1.036	0.045	0.991
$\sum\pi$[b]	6.001		6.069		6.010
total charge[c]					
C2	0.421	0.259	0.680	−0.063	0.617
O	−0.607	0.065	−0.542	0.056	−0.486
NH	−0.285	0.105	−0.180	0.087	−0.093
C4H	0.130	0.036	0.166	0.064	0.230
C5H	0.340	0.027	0.367	0.085	0.452
H2					0.281
BH_3			−0.492		

[a] Difference between the value of **5** and **6** or **7** and **5**, respectively. A negative value indicates a decrease. [b] Sum of π electron charges. [c] Hydrogen charges summed into heavy atom charges.

0.04 Å shorter than that of **1**; however, it agrees very well with that of an imidazol-2-ylidene−borane complex (1.599 Å).[2b]

The heterolytic dissociation energy D_e of **5** to give **6** and BH_3 is 53.5 kcal mol^{-1}. This is considerably higher than the D_e of $OC-BH_3$ (25.6 kcal mol^{-1}, although the C−B distance (1.534 Å) is shorter than in **5**)[12] and of H_3N-BH_3 (34.6 kcal mol^{-1})[12] and indicates a substantial thermodynamic stability of the B−C bond in **1**. The natural bond orbital analysis (NBO)[13] calculates a total charge of −0.492 at the BH_3 moiety in **4** and a Wiberg bond index for the C2−B bond of 0.887. Both values let us assume that the carbene−BH_3 bond has mainly covalent and charge transfer character similar to that of $OC-BH_3$.[12] Second-order perturbation theory analysis of the Fock matrix in the NBO basis shows hyperconjugation of the $\sigma(B-H_b)$ bonds into the empty $\pi^*(C2-N)$ and $\sigma^*(C2-N)$ orbitals and of the $\sigma(B-H_a)$ bond into the $\sigma^*(C2-O)$ orbital. These interactions sum up to 36 kcal mol^{-1} and indicate—compared to the overall complexation energy of 53.5 kcal mol^{-1}—a pronounced π bonding back donation from the BH_3 group to the carbene moiety. In Fischer-type transition metal carbene complexes, back donation from the metal fragment to the carbene also has been postulated.[14] Analogous back donation (although to a different extent) should occur in **1**. This contrasts with the interpretation of Fehlhammer et al., who conceived the C−B bonding in **4** to be of pure σ donor nature.[8]

Comparison of geometric parameters of **5** with those of **6** and **7** reveals that **5** takes an intermediate position between the two extremes, the carbene and the oxazolium ion (see Table 4). On going from **6** to **5** and to **7**, the C2−N and C2−O distances decrease markedly (the Wiberg bond indices increase correspondingly) and the

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(10) Structures **5**−**7** were optimized at MP2(FC)/6-31G* level using standard procedures and basis sets implemented in the GAUSSIAN 92 program package. Force constants were calculated at HF/6-31G* level and diagonalization of the force constant matrix showed **5** (C_s), **6** (C_s), and **7** (C_s) to be minima on the HF potential energy surface. GAUSSIAN 92: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, R. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, G.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. P. P.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1992. For a description of the basis set and methods, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(11) *Ab initio* calculations of a complex of imidazol-2-ylidene with borane have been reported previously: see ref 2b. For SCF-MO calculations of similar nucleophilic carbenes, see, e.g.: (a) Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457. (b) Sorensen, H. C.; Ingraham, L. L. *J. Heterocycl. Chem.* **1971**, *8*, 551. (c) Dixon, D. A.; Arduengo, A. J. *J. Phys. Chem.* **1991**, *95*, 4180. (d) Arduengo, A. J.; Dias, H. V. R.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 6812. (e) Sauers, R. R. *Tetrahedron Lett.* **1994**, *35*, 7213.

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(14) (a) Taylor, T. E.; Hall, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 1576. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, Germany, 1983; p 113.

N−C2−O angle widens by 7.6°; the angles around N and O decrease correspondingly. All other bonds and angles remain essentially unchanged. The widening of the N−C2−O bond is due to an increase of p orbital character in the C2 σ orbital which is a lone pair in **6** and a bonding orbital in **5** and **7** contributing to the C−B and the C−H bonds, respectively: **6** ($sp^{0.80}$), **5** ($sp^{0.94}$), and **7** ($sp^{1.50}$).[15]

Due to back donation from the BH_3 group, the total π electron density in the carbene fragment is higher in **5** (6.069 e^-) than in **6** (6.001 e^-) and in **7** (6.010 e^-). This excess of charge is mainly concentrated at C2; the π electron density at C2 increases from 0.463 e^- to 0.590 e^- on going from **6** to **5** (the total charge at C2 increases from +0.421 in **6** to +0.680 in **5** due to the electron-withdrawing influence of the BH_3 group in the σ framework). In contrast, only little π electron density is transferred from nitrogen to C2 (the π electron density at nitrogen decreases from 1.660 e^- in **6** to 1.620 e^- in **5** (the total NH charge decreases from −0.285 to −0.180). The π electron density at oxygen remains virtually unchanged (1.770 e^- in **6** and 1.753 e^- in **5**). The lack of pronounced charge transfer from nitrogen and oxygen to C2 together with the very small increase of the Wiberg bond indices of the C2−N and C2−O bonds (1.266/1.016 in **6** and 1.315/1.072 in **5**) indicates only a small increase of π bonding character in the N−C2−O moiety of the carbene fragment upon complexation with BH_3.

Although the differences in geometry between the borane complex **5** and the carbene **6** on the one hand and **5** an the oxazolium ion **7** on the other hand are almost equal (see Table 4), the electronic structure (charges, bond indices, C2 hybridization) of **5** resembles more that of the carbene **6**. Due to the lack of π back donation from H2 to C2 in **7**, the interaction of O and N atoms with the C2 center in enhanced: the (π) electron density at O and N decreases and the C2−N and C2−O indices of **7** are significantly higher than those in **5**. As a result, the π electron density at C2 is considerably higher in **7** than in **5**.

In total, the changes in geometry and electronic structure varies systematically on going from the carbene and its BH_3 adduct to the oxazolium ion. A similar trend has been observed in structures of imidazol-2-ylidene carbenes and their Lewis acid adducts.[2] However, the distortion of the carbene moiety in the protonated species **7** is much more pronounced than in the BH_3 complex. The latter resembles more the free carbene than the oxazolium ion. Only the π electron density at C2 is significantly enhanced in **5** due to back donation from the BH_3 group. Owing to this back donation, complex **4** and consequently **1** can be conceived as main-group Fisher-type carbene complexes.

Experimental Section

Synthesis of 1. Benzoxazole (120 mg, 1.00 mmol) was dissolved in a mixture of 2 mL of THF and 1.5 mL of ether under inert gas. After the addition of 0.63 mL of 1.6 M BuLi/hexanes solution at −110 °C, a white precipitate formed. The suspension was stirred for 10 min and then a solution of 245 mg triphenylborane (1.00 mmol) in 1 mL of THF and 4 mL of ether was added. The mixture became clear and was allowed to warm to room temperature. After a few minutes, precipitation of a white solid started. This solid can be filtered off and consists of lithium benzoxazol-2-yl borate with varying amounts of THF (as a ligand to lithium) depending on the degree of drying. However, for the synthesis of the carbene complex, the solvent of the suspension was evaporated *in vacuo* and a white residue was obtained. Hydrolysis with 5 mL of water, extraction with ether, and drying over $MgSO_4$ gave after solvent evaporation 125 mg of colorless crystals (35%). For X-ray crystallography, crystals were grown from methanol solution at room temperature, mp 139 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 7.05 (m, 3 H, *p*-*H*(Ph)), 7.14 (m, 6 H, *m*-*H*(Ph)), 7.21 (m, 6 H, *o*-*H*(Ph)), 7.54 (m, 2 H, benzoxazole-*H*), 7.72 (m, 1 H, benzoxazole-*H*), 7.95 (m, 1 H, benzoxazole-*H*), 14.75 (s, 1 H, N*H*). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 112.4 (*C*7), 114.9 (*C*4), 124.3 (*p*-*C*(Ph)), 126.6/126.7 (*C*5, *C*6), 126.9 (*m*-*C*(Ph)), 129.4 (*C*3a), 134.7 (*o*-*C*(Ph)), 149.9 (*C*7a), 154.0 (br, *ipso*-*C*(Ph), 197.5 (br, *C*2). IR (Nujol): 3295 (s, ν-NH). Anal. Calcd for $C_{25}H_{20}BNO$: C, 83.12; H, 5.58; N, 3.88. Found: C, 82.96; H, 5.67; N, 3.92.

X-ray Crystallography: Crystal Data for 1. The data were collected on a Stoe four-circle diffractometer at 153 K (Oxford Cryosystems) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structure was solved by direct methods and refined by full-matrix least-squares fitting based on F^2. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms isotropically using riding models (SHELXL-93, Sheldrick, G. M. University of Göttingen, 1993). Crystal data and details of the refinement can be found in Table 1.

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Supporting Information Available: A listing of crystallographic details and complete tables of bond distances, angles, atomic parameters, and isotropic and anisotropic thermal parameters (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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[15] Similar arguments hold true for the methylene carbene and the imidazol-2-ylidene carbene and their protonated derivatives: see ref 11c.