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# A Stable N-Heterocyclic Carbene with a Diboron Backbone

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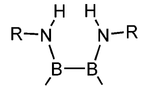
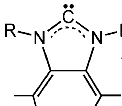
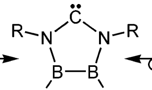
Stable N-heterocyclic carbenes[1] display a rich coordination chemistry and have found a multitude of applications as catalyst components due to their remarkable ligand properties.[2] Derivatives with various substitution patterns and ring sizes from four to six have been characterized, with the five-membered rings being by far the most common. A variety of inorganic analogues have been prepared as well, where the $N_2C$: moiety was replaced by isolobal fragments $N_2E$:, E = Si,[3a−c] Ge,[3c−e] Sn,[3c,f] $N^+$,[3g] $P^+$,[3h,i] $As^+$,[3i] or $Ga^-$.[3j,k]


**1**


**A**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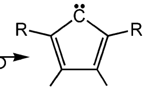
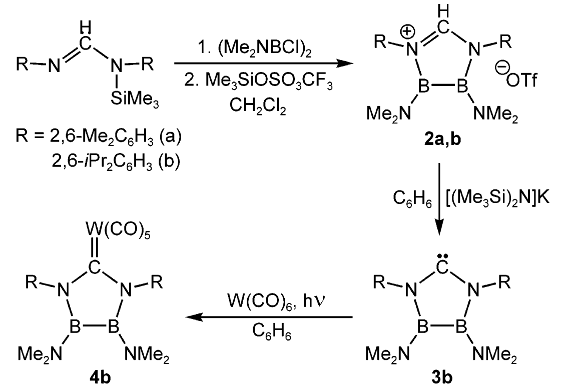

**B**

The growing significance of N-heterocyclic carbenes as spectator ligands in catalysis and our interest in five-membered inorganic heterocycles prompted us to investigate the stability of carbenes with inorganic backbones, as well as the influence of the inorganic backbone on the ligand properties of the carbon ligand. To our knowledge, only one N-heterocyclic carbene with an inorganic backbone (:$C(NR)_2PR'$) has been reported so far.[4]

Attempts to close a five-membered ring starting from known precursors of type **1**, with R = *t*Bu, 2,6-$Me_2C_6H_5$,[5] and carbon or even silicon fragments upon elimination of HCl or LiCl were not successful. However, the method used by Grubbs et al. for the synthesis of the first four-membered N-heterocyclic carbene[4a] easily generated, in high yield, the imidazolium precursor **2a**, which displayed $^1$H and $^{13}$C NMR signals corresponding to the ring proton and carbon at 7.93 and 175 ppm, respectively, as well as a $^{11}$B NMR signal at 31.3 ppm. Single-crystal X-ray diffraction revealed the expected structure featuring separated ions. The short endocyclic C−N bonds (1.335(3) and 1.316(3) Å) are consistent with electron delocalization over the N−C−N fragment, which is observed in all iminium analogues. The significant difference between the lengths of the endo- and exocyclic B−N bonds (1.511(3) and 1.521(3) Å vs 1.383(4) and 1.374(3) Å) indicates electron donation primarily from the exocyclic nitrogen to boron. As compared to imidazolium cations with a carbon framework, the B−B backbone is significantly longer (1.71 vs ca. 1.34 Å for C═C and ca. 1.51 Å for C−C backbone). The $B_2N_2C$ framework is a novel ring system. The only $B_2N_2C$ ring reported to date contains a coordinative bond between a borate and an ammonium moiety.[6]

Deprotonation of the precursor **2a** with potassium hexamethyldisilazide failed to generate the free carbene and led instead to a complex mixture of products that was not further investigated. The imidazole analogue **2b** containing the bulkier 2,6-diisopropylphenyl group was synthesized using the same method and subsequently yielded the free carbene **3b** in 65% isolated yield according to Scheme 1. The carbene was isolated as a pale yellow powder with good solubility in benzene, toluene, and THF. Rapid decomposition was observed in $CH_2Cl_2$. Neither the solid nor the solutions of **3b** showed any signs of decomposition when stored for a few weeks at room temperature in an inert atmosphere; however, the B−N bonds hydrolyzed rapidly in air, generating the corresponding amidine. The NMR spectra displayed the expected signals, most notably the singlet in the $^{11}$B NMR corresponding to the backbone boron atoms at 33.2 ppm and the $^{13}$C NMR signal for the carbene carbon at 304 ppm. This value corresponds to the highest downfield shift reported for a diaminocarbene. Large, pale yellow crystals were obtained by cooling a solution of the carbene in a 1:1 hexane/toluene mixture.

***Scheme 1.*** Synthesis and Coordination of $B_2$-Backbone Carbene



Compound **3b** crystallizes as a modulated structure that presented significant difficulties in the structural refinement. In the primary cell the structure was modeled as consisting of fully disordered molecules across a 2-fold axis. The carbene ring (Figure 1) is nearly planar. As compared to diaminocarbenes with a carbon backbone, the relatively long B−B bond does not result in a very significant opening of the N1−C1−N2 angle (108.45(8)° vs 101−106° and 106−108°, respectively). However, it has a notable effect on the phenyl groups, which form an unusually small dihedral angle, thereby protecting the carbene carbon. The N2−C12 and N5−C24 bonds form an angle of only 120.5° (phenyl−phenyl dihedral angle 121.3°), as compared to 145−146° in analogues with a C═C backbone.[7] Similarly to **2a**, the endocyclic B−N bonds in **3b** are ca. 0.1 Å longer than their exocyclic counterparts. This suggests little electron donation from nitrogen to boron within the ring skeleton and indicates the similarity with the isolobal organic framework **A** rather than **B**. The hindered rotation around the exocyclic B−N bond is confirmed by the nonequivalence of the methyl groups on nitrogen in the room temperature $^1$H and $^{13}$C NMR spectra.

To assess the coordinative properties of the novel carbene, its behavior toward selected transition metal complexes was investigated. The reaction of **3b** with $(PhCN)_2PdCl_2$ led to a complex

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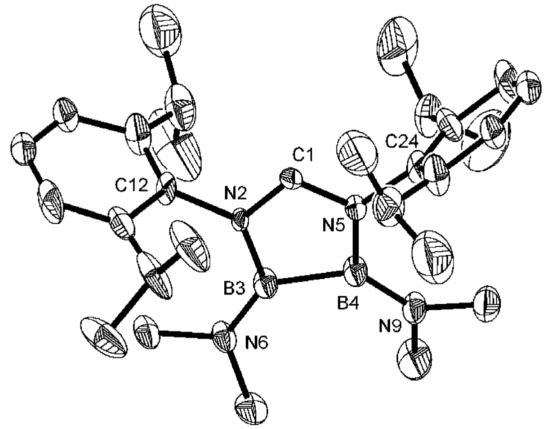

***Figure 1.*** ORTEP-like diagram of **3b** at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N5−C1 1.352(1), N2−C1 1.404(1), N2−B3 1.460(2), N5−B4 1.470(2), B3−B4 1.731(2), B3−N6 1.380(2), B4−N9 1.374(2); N2−C1−N5 108.45(8), C1−N2−B3 116.70(9), C1−N5−B4 114.84(9), N2−B3−B4 98.01(9), N5−B4−B3 101.79(9).

mixture of products, whereas no reaction was observed with $[Cp^*RuCl]_4$ in THF. The latter reagent is known to react quickly with N-heterocyclic carbenes, yielding deep blue complexes.[8]

The UV-promoted reaction of **3b** with tungsten hexacarbonyl produced the expected pentacarbonyl derivative **4b**, which was readily crystallized from benzene. The reaction proceeded quantitatively in benzene, whereas in tetrahydrofuran only formation of $(CO)_5W(thf)$ was observed. The signal for the carbene carbon in the $^{13}C$ NMR spectrum shifted upfield upon coordination to 259.1 ppm. The observation of $^{183}W$ satellites ($^1J_{WC}$ 110.5 Hz) confirms the W−C bond formation. The $A_1^{(2)}$ stretching vibration of the $W(CO)_5$ moiety was observed at 2054 $cm^{-1}$, at a lower wavenumber compared to those of the related N-heterocyclic carbene complexes (2060−2065 $cm^{-1}$).[9] This observation, along with the high value of the $^1J_{WC}$ coupling constant for the carbene carbon in comparison to similar complexes containing five-membered N-heterocyclic carbenes with a carbon backbone (95−96 Hz),[9c] indicates that **3b** is a better $\sigma$-donor than classical carbenes. Its low reactivity is probably influenced by the very efficient protection of the carbene carbon by the diisopropylphenyl groups.

The crystal structure of **4b** (Figure 2) reveals the expected octahedral geometry at tungsten, with one coordination site occupied by the carbene. The metal as well as the axial and two equatorial CO groups lie in the plane of the carbene ring. Except for a dramatic opening of the dihedral angle between the planes of the phenyl rings to 157.9°, no significant changes in the metric parameters of the carbene occur upon coordination. The steric repulsion between the carbonyl and the diisopropylphenyl groups also causes the equatorial carbonyl groups lying in the carbene plane to be notably bent toward the axial position (C1−W1−C4 163.3(2)° vs C2−W1−C5 179.4(2)°). The C6−W1 bond length of 2.283(4) Å is similar to the values found for other tungsten diaminocarbene complexes.

The fact that **3b** is a better $\sigma$-donor than classical carbenes demonstrates the potential of carbenes with an inorganic backbone as ligands in transition metal chemistry, as well as the major influence of the inorganic backbone on the coordination ability of the carbon ligand. The synthesis of analogues with less bulky substituents on the nitrogen atoms adjacent to the carbene carbon is currently being investigated.

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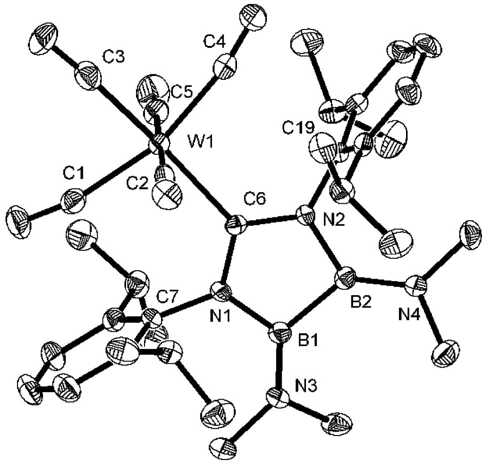

***Figure 2.*** ORTEP-like diagram of **4b** at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): W1−C6 2.283(4), N1−C6 1.384(5), N2−C6 1.382(5), N1−B1 1.482(5), N2−B2 1.499(5), B1−B2 1.700(7), B1−N3 1.398(6), B2−N4 1.394(6), C3−W1 1.991(5), $C_{eq}$−W1 2.036(5)−2.040(5); N1−C6−N2 109.2(3), C6−N1−B1 114.5(3), C6−N2−B2 114.3(3), N1−B1−B2 101.0(3), N2−B2−B1 100.0(3).

**Supporting Information Available:** Experimental details and complete spectroscopic data for **2**−**4**; crystallographic details including CIF files for **2a**, **3b**, and **4b**; and the complete ref 9c. This material is available free of charge via the Internet at http://pubs.acs.org.

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