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ORIGINAL PAPER

A Diamidocarbene-Supported Aminoborylene: Characterization and Discussion of the Elusive Crystal Structure

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Abstract
Five years after we published the synthesis of the first diamidocarbene (DAC)-supported amino borylene **4**, we now report the elusive single crystal X-ray structure. The X-ray structure of **4** was found to corroborate our previous computational studies which indicated that the borylene adopted a heterocumulenic geometry with a near linear $C_{(carbene)}=B=N$ unit (175.88(18)°) as well as short C = B and B = N distances of 1.416(3) and 1.344(3) Å, respectively. Additionally, we further provide a qualitative and quantitative discourse on said structure with respect to the precursor compounds used to prepare **4** as well as to the known cyclic (alkyl) amino carbene (CAAC) analog **2.**

Keywords *Borylene · Diamidocarbenes · Main group chemistry · Low valent*

Introduction

The isolation of the first carbene stabilized borylene (**1**, Fig. 1) by Bertrand in 2011 was a landmark achievement in the area of low valent boron chemistry [1]. Compound **1** represented the first example of a three-coordinated boron atom that was isoelectronic with simple Lewis bases such as amines. Like simple Lewis bases, **1** was found to undergo 1-electron oxidation to give rise to stable radical cations, and was also protonated using triflic acid [1]. Since that seminal report, several groups including our own have actively explored the isolation of increasingly lower coordinate carbene-stabilized borylene compounds including the dicoordinated analogues **2**, **3** and **4** from the groups of Bertrand [2], Braunschweig [3], and Hudnall [4], respectively. In 2014, it was shown that compound **2** could be viewed as both a carbene-stabilized aminoborylene (based on reactivity) and a heteroallene (based on the solid state structure) [2]. Remarkably, **2** was capable of splitting dihydrogen across the C = B unit and even coordination of carbon monoxide to the boron atom [2]. Similarly, Braunschweig demonstrated that **3** could be generated *in situ* and trapped with carbon monoxide [3a]. But, what is perhaps most impressive was the ability of borylene **3** to trap and even couple dinitrogen under appropriate conditions[3b, 3c]. In 2016, we followed up on Bertrand's report of **2** and isolated the diamidocarbene (DAC)-supported aminoborylene **4** [4]. However, single crystals suitable for an X-ray diffraction analysis were elusive at that time. In lieu of crystals, we optimized the structure of **4** and computed the ^{11}B NMR chemical shift for the compound using DFT methods and found that the predicted structure was the heterocumulene as described in Fig. 1 [4]. Herein we now report the single crystal X-ray structure of **4** which corroborates our computational findings; we further provide a qualitative and quantitative discourse on said structure with respect to precursor compounds and the known analog **2**.

Single Crystal X-ray Crystallography

An orange block-like crystal of **4** with dimensions $0.37\times0.24\times0.20$ mm^3 was secured to a Mitegen mount using Paratone oil and its single crystal X-ray diffraction

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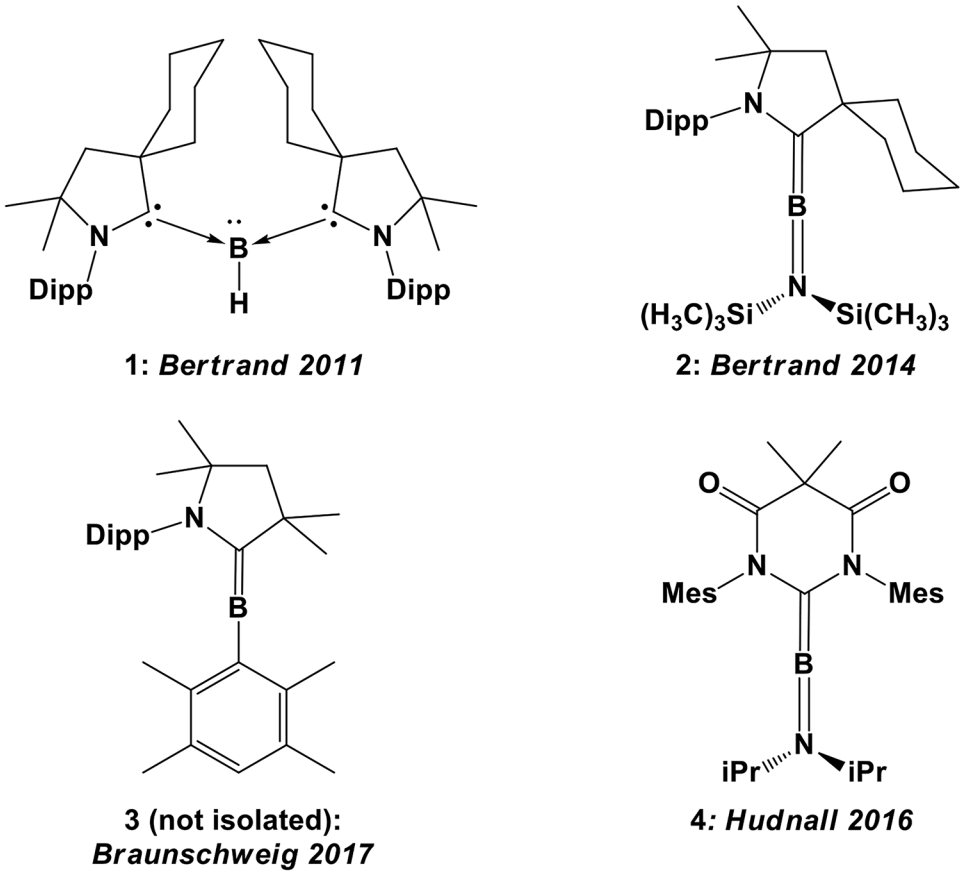

Fig. 1 Known examples of dicoordinated carbene-supported borylenes

data was collected at 100 K using a Rigaku AFC Kappa diffractometer equipped with a Saturn 724 CCD detector and graphite-monochromated Mo $K_{\alpha 1}$ ($\lambda = 0.71073$ Å) radiation. A data collection strategy to ensure maximum data redundancy and percent completeness was determined via CrystalClear. Unit cell determination, initial indexing, data collection, frame integration, Lorentz-polarization corrections, and final cell parameter calculations were carried out using CrystalClear. Multi-scan absorption corrections were performed using REQAB [5]. The crystal structure was solved via intrinsic phasing methods using ShelXT and refined using ShelXL in the Olex2 graphical user interface [6]. The space group was unambiguously verified by PLATON [7]. The final structural refinement included anisotropic temperature factors on all constituent non-hydrogen atoms. Hydrogen atoms were attached via the riding model at calculated positions using suitable HFIX commands. The crystallographic and refinement data for **4** is listed in Table 1.

Results and Discussion

In our original submission on the synthesis of the aminoborylene **4**, we were unable to obtain single crystals of this compound suitable for a single crystal X-ray diffraction analysis. This was primarily due to the instability of **4** in solution over time (even at low temperature). Interestingly, the neutral radical **6**˙ (*vide infra*), which is a synthetic precursor to **4**, was found to be much more stable than the borylene. We ultimately decided to publish the synthesis of **4** without the X-ray structure. Over the past few years, we continued to attempt to grow single crystals of **4**, and were finally successful by rapidly crystallizing the molecule out at low temperature (-35 °C) from a 3:1 THF:hexanes mixed solvent system inside the freezer of our glove box. The crystals were separated from the solvent and suspended in a dry mixture of mineral and Paratone oils inside the box for transfer to the diffractometer.

The solid structure of **4** (Fig. 2) crystallized in the centrosymmetric monoclinic space group $P2_1/c$ and contained one molecule as the contents of the asymmetric unit. Within **4**, the coordination environment around the carbene carbon (C1) is distorted trigonal as evidenced by the angles of 113.37(13)°, 123.38(15)°, and 123.20(15)° which

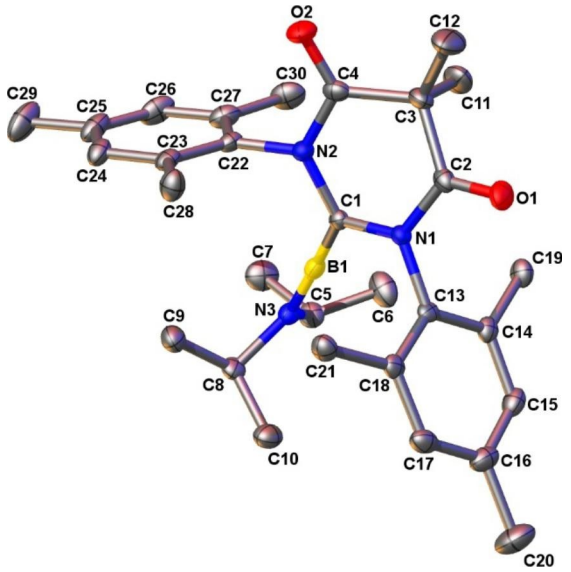

Fig. 2 Anisotropic displacement ellipsoid plot of **4** with ellipsoids set to the 50% probability level. Hydrogen atoms have been removed for the sake of clarity

correspond to the N1-C1-N2, N2-C1-B1, and N1-C1-B1 angles respectively.

To further investigate the structure of aminoborylene **4**, we compared the metrical parameters to those previously reported by our group for $\mathbf{5}^{+}$ (the DAC-supported borenium cation) and $\mathbf{6}^{\cdot}$ (the DAC-supported boryl radical) which were used to prepare the borylene via two sequential 1-electron reductions (Fig. 3) [4]. Upon each reduction, it was proposed that increased π-bonding character would build up between the C1 and B1 atoms. Consistent with this notion, the C1-B1 bond distance in **4** (1.416(3) Å) was found to be less than that observed in the structures for both $\mathbf{5}^{+}$ (1.641(4) Å) and radical $\mathbf{6}^{\cdot}$ (1.577(3) Å) (Fig. 3) and is consistent with multiple bond character between C1 and B1 [4]. Within **4**, the B1-N3 bond was measured to be 1.344(3) Å and is shorter than that from the borenium salt $\mathbf{5}^{+}$ (1.365(4) Å) and the radical **6** (1.376(3) Å) [4] and is also consistent with some degree of π-bonding. The C1-B1-N3 angle within **4** was measured at 175.88(18)°, which clearly revealed the linear dicoordinated nature of the boron atom when compared to the three coordinated, trigonal planar boron atoms in the

Table 1 Crystallographic and refinement data for compound **4**

CCDC deposition number	2162278
Empirical formula	$C_{30}H_{42}BN_3O_2$
Formula weight/g·mol^{-1}	487.47
Temperature/K	100(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.2660(7)
b/Å	17.7938(12)
c/Å	17.2473(13)
α/°	90
β/°	97.036(4)
γ/°	90
Volume/Å^3	2822.3(4)
Z	4
ρ_{calc}/g·cm^{-3}	1.147
μ/mm^1	0.071
$F(000)$	1056
Crystal size/mm^3	0.37 × 0.24 × 0.20
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.286 to 52.744
Index ranges	-11 ≤ h ≤ 10, -22 ≤ k ≤ 22, -20 ≤ l ≤ 21
Reflections collected	37606
Independent reflections	4250 [R_{int} = 0.0735, R_{sigma} = 0.0488]
Data/restraints/parameters	5759/216/337
Goodness-of-fit on F^2	1.032
Final R indices [$I \geq 2\sigma(I)$]	R_1 = 0.0494
	wR_2 = 0.1198
R indices (all data)	R_1 = 0.0727
	wR_2 = 0.1307
Largest diff. peak/hole/e·Å^{-3}	0.63/-0.23

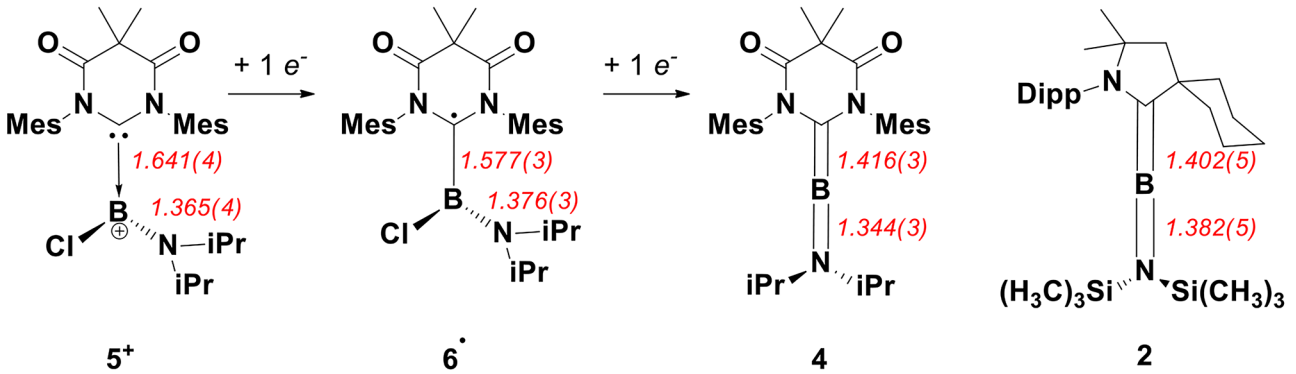

Fig. 3 Comparison of metrical parameters for compounds $\mathbf{5}^{+}$, $\mathbf{6}^{\cdot}$, **4**, and **2** obtained from their respective single crystal X-ray diffraction data

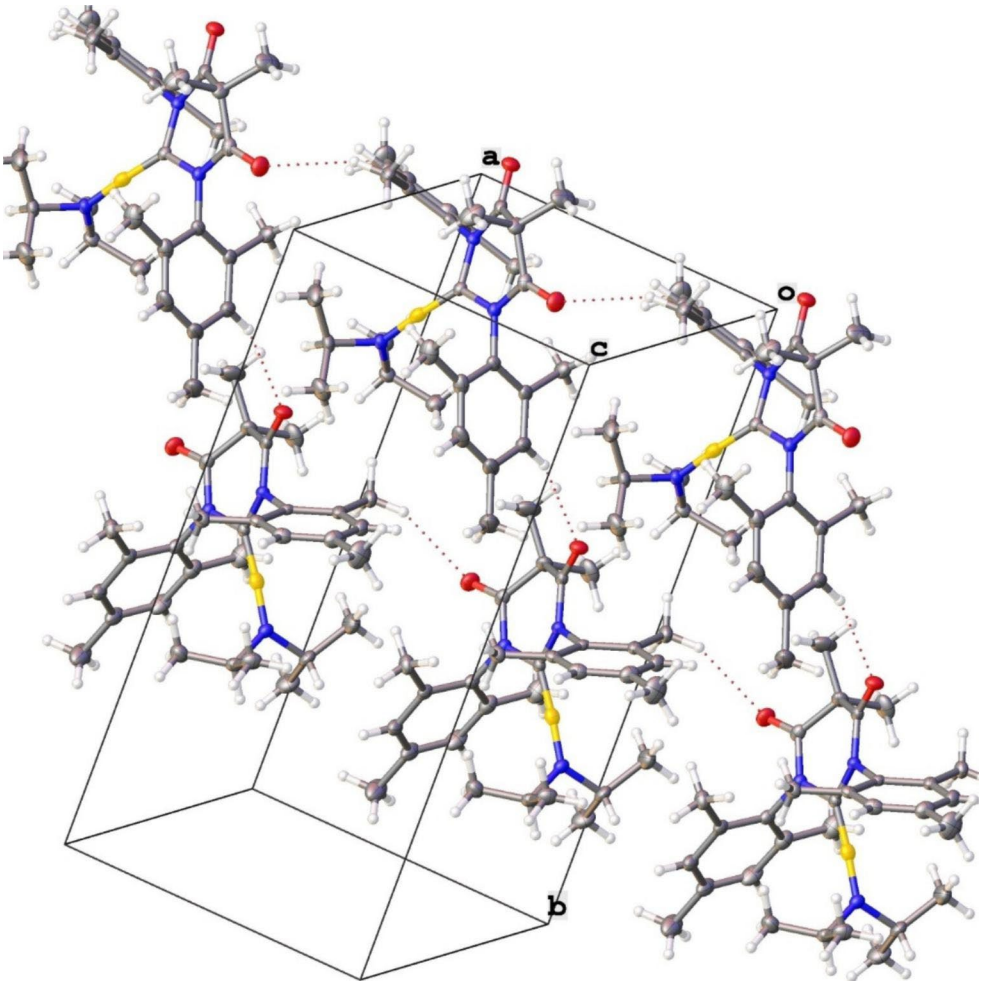

Fig. 4 Packing diagram of **4** with ellipsoids set to the 50% probability level. C-H•••O contacts furnishing supramolecular stability between the neighboring molecules and helices are denoted by dashed lines

borenium $\mathbf{5}^{+}$ and the neutral radical $\mathbf{6}^{\cdot}$, (C1-B1-N3 angles of 125.8(2)° and 127.7(2)° respectively) [4].

This dramatic structural change around the boron atom can be attributed to a change in its coordination environment upon the sequential two electron reduction. The linear C1-B1-N3 linkage within **4** is consistent with a pseudo allenic structure (double bonds between the boron atom and both the carbene carbon and nitrogen) [4]. This allenic structure was further confirmed by examining the dihedral angle between two planes defined as plane 1 (N1-B1-N2) and plane 2 (C5-B1-C8). The dihedral angle between the centroids of planes 1 and 2 was found to be (92.61(11)°) which clearly illustrates that the *iso*propyl substituents on the N3 atom are orthogonal to the N1-C1-N2 π-system in the DAC ligand. Structural parameters (i.e. bond distances and angles) for the DAC within **4** are similar to those for the DAC in both the borenium $\mathbf{5}^{+}$ and the neutral radical **6** [4]. Consistent with the crystallographic data, the multinuclear NMR spectroscopic data obtained for borylene **4** are also indicative of a hetero allenic structure. For example, the ^{1}H NMR of **4** is highly symmetric with only a single aromatic CH resonance (6.66 ppm), a single $C(CH_3)_2$ resonance from the DAC backbone methyl groups (1.99 ppm), and a single set of signals for equivalent isopropyl substituents on the amino nitrogen (a septet at 2.48 ppm and a doublet at 0.43 ppm). The ^{11}B NMR signal observed for borylene **4** at 62 ppm was also significantly deshielded when compared to precursor $\mathbf{5}^{+}$ (23.4 ppm) which can be rationalized on the basis of a change in hybridization at the boron center from pseudo sp^2 to sp.

Next, the structural features for **4** were compared to those from the CAAC-supported borylene (**2**) reported by the Bertrand group in 2014 [2] (Fig. 3, far right). In the case of compound **2**, the B-C and C-N bond distances were found to be 1.402(5) Å and 1.382(5) Å, respectively compared to 1.416(3) Å and 1.344(3) within **4** [2]. The C-B-N bond angle within the CAAC-aminoborylene **2** was measured at a slightly-less linear value of 174.7(3)° when compared to that of **4** (175.88(18)°) [2]. The differences in bond angles and distances between the **2** and **4** complexes can be rationalized on the basis of increased π-acidity in going from CAAC to DAC.

Finally, it was observed that the solid state integrity between neighboring, symmetry-equivalent molecules

within the crystal is maintained by an array of C-H•••O contacts. Relative to the crystallographic *c*-axis, molecules are related to one another by the 2_1 screw axis forming helices. Neighboring helices are related to one another via translations parallel to the *a*-axis. Within the helices, integrity is maintained by C-H···O (d(C24···O1) ~ 3.35 Å; Θ(C24-H24-O1) ~ 153°) contacts between neighboring molecules. C-H···O (d(C19···O2) ~ 3.48 Å; Θ(C19-H19C-O2) ~ 153°) contacts along the *a*-axis furnish stability between neighboring helices (Fig. 4).

Conclusions

Herein we reported the elusive single crystal X-ray structure of the DAC-supported aminoborylene, **4**, which our lab synthesized in 2016. Gratifyingly, the solid state structure of **4** was in agreement with the calculated structure that we previously disseminated, i.e. the C1-B1-N3 unit adopts a hetercumulene structure with a near linear C1-B1-N3 linkage (175.88(18)°) and orthogonal C1-B1 and N3-B1 π-systems (dihedral angle = 92.61(11)°). The metrical parameters of **4** were also compared with those obtained on precursor molecules $\mathbf{5}^{+}$ and $\mathbf{6}^{\cdot}$ as well as a CAAC-supported aminoborylene (**2**) reported previously.

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Data Availability The CCDC file 2,162,278 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Declarations

Statements and Declarations The authors declare no competing financial interest.

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