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Iminoborane Adducts

# The Reactivities of Iminoboranes with Carbenes: BN Isosteres of Carbene–Alkyne Adducts**

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***Abstract:*** *The first examples of adducts of cyclic alkyl(amino) carbenes (CAAC) and N-heterocyclic carbenes (NHCs) with iminoboranes have been synthesized and isolated at low temperature (−45 °C). The adducts show short B=N bonds and planarity at boron, mimicking the structures of the isoelectronic imine functionality. When di-tert-butyliminoborane was reacted with 1,3-bis(isopropyl)imidazol-2-ylidene (IPr), the initially formed Lewis acid–base adduct quickly rearranged to form a new carbene substituted with an aminoborane at the 4-position. Warming the iminoborane–CAAC adduct to room temperature resulted in an intramolecular cyclization to give a bicyclic 1,2-azaborilidine compound.*

Since Arduengo's 1991 report of the synthesis and isolation of 1,3-bis(adamantyl)imidazol-2-ylidene (**I**),[1] stable N-heterocyclic carbenes (NHCs) have become useful, and often essential, components of the modern chemist's toolbox.[2] A wide variety of stable carbenes are now available, with each offering slightly different electronic properties and reactivity patterns. For example, diamino-NHCs, with nitrogen at the 1- and 3-positions of the ring (such as **I**), showed no reactivity in reactions with CO, while cyclic alkyl(amino)carbenes **II**[3] quickly coordinated CO to form ketene **III**.[4] Though not active with the triple bond in CO, diamino-NHCs were found to react with polarized alkynes, adding to the C–H terminus of HC≡C-B(Mes)$_2$ to give the zwitterionic compound **IV** (Figure 1).[5]

For some time, our group has been interested in the chemistry of iminoboranes (RB≡NR),[6,7] which contain a polarized triple bond akin to those in CO and HC≡C-BMes$_2$. Despite the frequent use of NHCs in conjunction with other unsaturated diboron species,[8] the reactivity of iminoboranes with carbenes has not been explored. Herein we communicate the preliminary results of a study consisting of the reactions of di-*tert*-butyliminoborane (**1**) with three singlet carbenes.

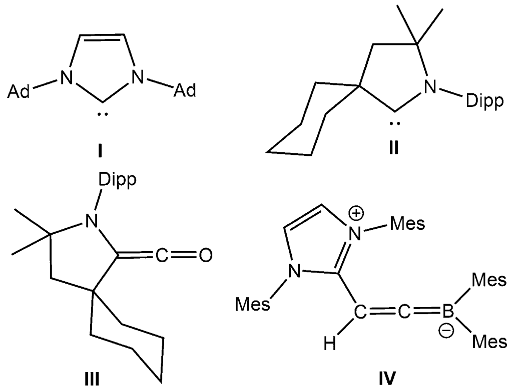
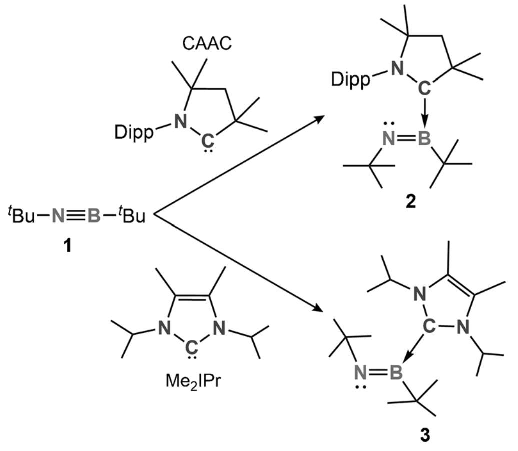


***Figure 1.*** Examples of stable NHCs and their reactions with triple bonds. Ad = adamantyl, Dipp = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl.

When equimolar quantities of **1** and either CAAC or Me$_2$IPr were allowed to react in pentane at −45 °C, adducts **2** and **3** were obtained in high yields (95 %, Scheme 1). In a similar fashion to the formation of **III** and **IV**, attack of the carbene at the electropositive end of the triple bond induced the movement of one pair of π-electrons out of their original orbitals, shifting them to the opposite end of the molecule. Both compounds were extremely sensitive to air and moisture, but could be stored in the solid state for several weeks under argon at −45 °C without decomposition.



***Scheme 1.*** Synthesis of compounds **2** and **3**. Both reactions were run at −45 °C in pentane.

The $^{11}$B NMR spectra of **2** and **3** feature signals at $\delta$ = 22 ppm and 24 ppm, respectively, which are shifted considerably downfield with respect to that of **1** ($\delta$ = 5 ppm). In both cases, the $^{13}$C NMR spectra revealed the loss of the carbene

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signal and the appearance of a new peak at $\delta = 194.1$ ppm for **2** and $\delta = 164.8$ ppm for **3**. Similarly, the IR spectra of **2** and **3** showed the disappearance of the B≡N stretch[9] at $\tilde{\nu} = 2018\ \text{cm}^{-1}$ concomitant with the appearance of B=N vibrations at $\tilde{\nu} = 1666\ \text{cm}^{-1}$ (**2**) and $1556\ \text{cm}^{-1}$ (**3**). Both the $^{11}$B NMR shift and the B=N stretching vibrations qualitatively agree with simulations based on DFT analysis (Table S1).

Crystals suitable for single-crystal X-ray crystallography were grown from cold, concentrated solutions of **2** and **3**. The results of X-ray analyses reveal the coordination of the CAAC and NHC to the boron atom of the iminoborane (Figure 2). Perhaps the most striking difference between the two structures is in the conformation of the two bulky *tert*-butyl groups about the B=N bond. In **3**, the two groups adopt the expected *trans* configuration; however, in **2**, these two bulky groups sit on the same side of the B=N bond. Additionally, the C1-B1-N1 angle in **3** measures 123.7(3)°, which is in the expected range for three-coordinate boron, but in **2** this angle is very acute, 93.9(1)°. The seemingly odd geometry of **2** is explained by DFT analysis, which shows a pronounced interaction between the lone pair on the nitrogen of the B=N unit and the empty p orbital on the carbene carbon of CAAC (Figure S1). The distance between C1 and N1 measures 2.196 Å, and NBO analysis of **2** indicates a weak bonding interaction, with a Wiberg bond order of 0.29. The B−N bond length in **2** (1.330(2) Å) and **3** (1.340(5) Å) is slightly longer than that in **1** (1.258(4) Å),[9] as expected to accompany a decrease in bond order. The trigonal-planar geometry at the boron atoms of both complexes is indicated by the sum of angles about the boron, measuring 360° for both compounds.

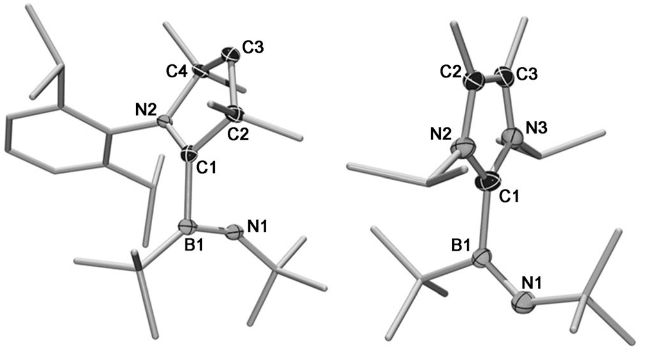


***Figure 2.*** Molecular structures of **2** (left) and **3** (right). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and some ellipsoids are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: B1–N1 1.330(2), B1–C1 1.660(3), N2–C1 1.336(2), N2–C4 1.5257(19), C4–C3 1.529(2), C3–C2 1.547(3), C1–C2 1.549(2); N1-B1-C1 93.9(1), N2-C1-C2 107.51(14), N2-C4-C3 99.36(13), C4-C3-C2 106.56(13). **3**: B1–N1 1.340(5), B1–C1 1.648(4); N1-B1-C1 123.7(3), N2-C1-B1 126.1(2).

When **1** was reacted with 1,3-bis(isopropyl)imidazol-2-ylidene (IPr) at −45 °C, an initial peak at $\delta = 23$ ppm in the $^{11}$B NMR spectrum gradually gave way to a new resonance at $\delta = 42$ ppm. The final product, which was isolated as a white solid, showed both a one-proton singlet at $\delta = 4.61$ ppm in the $^{1}$H NMR spectrum (N-H) and a signal for the free carbene (C2) at $\delta = 210.2$ ppm in the $^{13}$C NMR spectrum. These data suggested that the product was not the expected adduct, but instead a free carbene in which **1** had inserted into one of the C−H bonds in the carbene backbone. This was confirmed by single-crystal X-ray diffraction (Figure 3b), which showed **5** as the product of insertion at the 4-position of IPr, generating an aminoborane. DFT/GIAO calculations on the presumed intermediate (**4**) predicted an $^{11}$B NMR shift of $\delta = 24$ ppm, in good agreement with the initial peak at $\delta = 23$ ppm, supporting the plausibility of the reaction scheme presented in Figure 3a. The computed energetics of the rearrangement are presented in Figure S2. The energy of compound **5** was calculated to be lower than that of the normal carbene–BN adduct (such as in **2** and **3**) by 4.1 kcal mol$^{-1}$. Compound **5** is air- and moisture-sensitive and readily dissociates in the solid state at −35 °C, within a few days, spontaneously forming dimerized 1,3-diaza-2,4-diboretidine[10] and free carbene ($\Delta G_{298.15} = -5.8$ kcal mol$^{-1}$, Table S2)

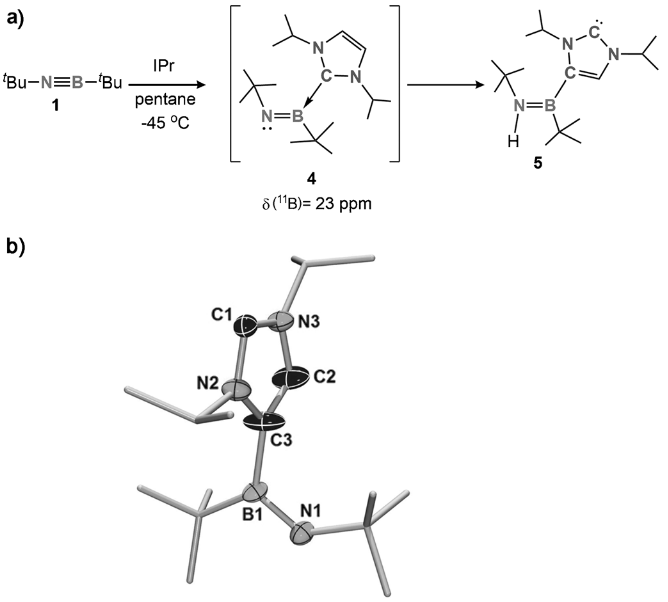
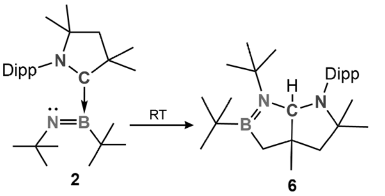


***Figure 3.*** a) Synthesis of **5**. b) Molecular structure of **5**. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and some ellipsoids are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–N1 1.397(1), B1–C3 1.621(7); N1-B1-C3 119.1(4), N2-C3-B1 126.1(4).

Processes are known by which the backbones of metal-free NHCs are functionalized by migration of groups presumably first bound at the carbene carbon. In 2009 Gates et al. reported such a rearrangement in which reaction of a phosphaalkene with an NHC resulted in the formation of a 4-phosphino-substituted NHC.[11] Silylation at C4 has also been observed through the migration of silyl substituents to the NHC backbone.[12] Such a process was postulated by Arduengo et al. to be at work in the chlorination of the NHC backbone with carbon tetrachloride.[13] Compound **5** is the first example of an NHC substituted with an aminoborane at the 4-position; its reactivity is currently being explored in our lab.

As mentioned, adducts **2** and **3** were unstable at temperatures above $-45\,°C$.[14] In the case of **3**, dissociation of the carbene followed by cyclodimerization of **1** was observed, in accord with the calculated spontaneity of this transformation ($\Delta G = -16.0\ \mathrm{kcal\,mol^{-1}}$, Table S2). When **2** was held at room temperature, an intramolecular cyclization giving an azaborolidine compound (**6**) was observed [Eq. (1)]. The $^{11}$B NMR spectrum of **6** showed a broad signal at $\delta = 51$ ppm, which falls in the expected range for chemical shifts reported for similar cyclic boron compounds[15] and closely matches a DFT/GIAO $^{11}$B NMR signal calculated for the optimized structure of **6** ($\delta = 54$ ppm, Table S1). $^{1}$H NMR analysis of **6** showed splitting of the methyl group resonances into three singlets at $\delta =$ 1.57, 1.28, and 0.84 ppm, emergence of methylene protons at $\delta = 1.99$ ppm, and the presence of a single $C_{carbene}$–H resonance at $\delta = 5.19$ ppm, all consistent with the proposed structure of **6**. A proposed mechanism for the transformation is discussed in Figure S3.



(1)

Colorless crystals of **6** suitable for X-ray diffraction were grown from a saturated pentane solution at $-30\,°C$ (Figure 4). The B1–N2 bond of **6** (1.418(2) Å) is within the standard range for B=N bonds, and the B1–C26 distance of 1.588(2) Å is considerably shorter than the carbene–boron bond in **2** (1.660(3) Å), indicating a formal conversion of the dative bond (coordinate covalent) to a conventional covalent (electron-sharing) interaction. Even though intramolecular rearrangements of this type are relatively common in NHC chemistry, only one example has been reported involving a CAAC.[16]

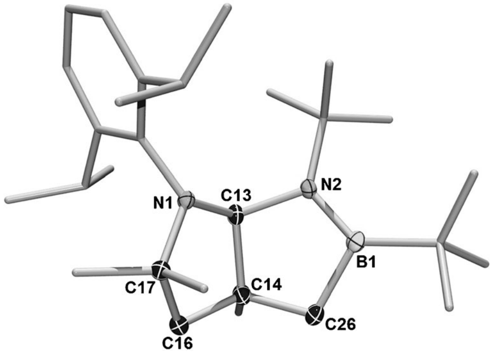
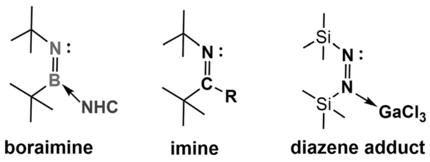


*Figure 4.* Molecular structure of **6**. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and some ellipsoids are omitted for clarity. Selected bond lengths [Å] and angles [°]: B1–N2 1.418(2), C13–C14 1.552(2), B1–C26 1.588(2), C13–N1 1.477(2), C17–N1 1.500(2), C14–C26 1.542(2), C14–C16 1.528(2); N1-C13-N2 115.8(1), C13-N2-B1 111.6(1), N2-B1-C26 106.9(1).

The literature on five-membered azaboracycloalkanes is sparse, with only a few reported syntheses.[17] In this context, this reaction represents an elegant route to a 1,2-azaborolidine derivative via the intramolecular rearrangement of a CAAC–iminoborane adduct.

In conclusion, we have prepared and structurally characterized examples of an until recently unknown class of iminoborane–carbene adducts,[18] as well as a new BN-functionalized carbene. Adducts **2** and **3** are new members of an emerging group of compounds in which the use of boron and a two-electron donor (such as an NHC) replaces carbon and a one-electron donor in the syntheses of inorganic analogues of conventional unsaturated organic functional groups. The structural similarities between the organic functionalities and the boron-based analogues are not replicated by analogues constructed of the larger members of Group 14, which tend to exhibit poor π-bonding and lone pair density at the heavy element.[19] The recent characterization of a Lewis acid adduct of a diazene[20] furthers this analogy, strengthening the conceptual ties between isoelectronic compounds constructed of light p-block elements. It seems not a stretch to term compounds **2** and **3** “boraimines”, as structural and isoelectronic congeners of the conventional imine functional group. The room-temperature rearrangements yielding **5** and **6** serve to add to the stock of functionalized carbenes available for experimentation and synthesis (in the case of **5**) and open a route to 1,2-azaborolidine derivatives (such as **6**).



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[21] CCDC 1024624 (**2**), 1024641 (**3**), 1024639 (**5**), and 1024628 (**6**) contain 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.