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N-Heterocyclic Olefin Stabilized Borenium Cations

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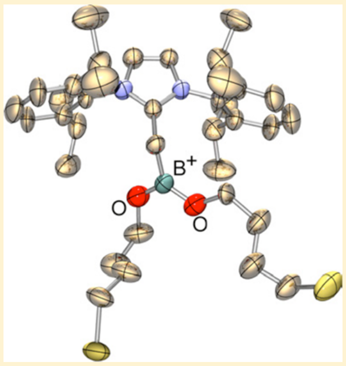
Supporting Information

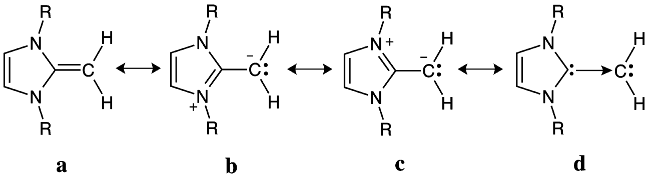
ABSTRACT: The reaction of the N-heterocyclic dicarbene (NHDC) $[:C\{[N(2,6\text{-}Pr^i_2C_6H_3)]_2CHCLi(THF)\}]_n$ with iodomethane, in a hexane/THF mixture, affords the ylidic N-heterocyclic olefin NHC═CH_2 (**1**; NHC = $:C\{N(2,6\text{-}Pr^i_2C_6H_3)CH\}_2$) in high yield. The reaction of **1** with BBr_3 in hexane gives the neutral compound NHC−CH_2:BBr_3 (**2**), which in THF unexpectedly converts to the borenium salt $[NHC{-}CH_2{:}B\{O(CH_2)_4Br\}_2]^+[Br]^-$ (**3**) through ring opening of THF.



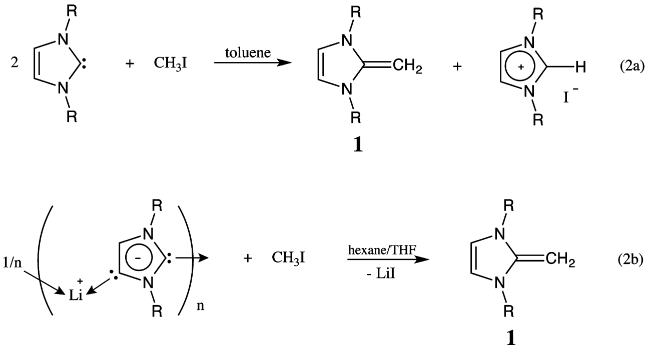
As potent Lewis acids, the three-coordinate borenium cations L:BR_2^+ (L: = Lewis base donor ligand; R = σ-bound substituents) are of considerable interest, due to their enormous potential in organic synthesis and catalysis.[1−6] The chemical behavior of borenium cations can be substantially influenced by electronically tuning both the R substituents and the L: ligand. For example, a heteroatom (i.e., N or O)-containing R substituent could enhance the stability of a borenium cation by donating the lone pair of electrons of the heteroatom to the vacant p orbital of the cationic boron center.[7,8] Consequently, the synthesis of the long-pursued dihydrido borenium species was a significant achievement.[9] In a similar fashion, the electrophilicity and stability of borenium cations may be affected by manipulating the electronic and steric properties of the Lewis base (L:). Thus, incorporating versatile ligands such as N-heterocyclic carbene based moieties into borenium systems[4,10−14] is promising from both synthetic and catalytic perspectives. Indeed, N-heterocyclic carbene based borenium cations have been not only utilized in hydrogen activation and hydrogenation catalysis[4] but also postulated to catalyze hydroboration of alkenes.[15]

N-heterocyclic carbenes, as iconic Lewis bases, may be considered ylidic N-heterocyclic olefins (NHOs) if the bridgehead C2 carbon atom is capped by a methylene unit, :CH_2. Resonance forms **b**−**d** (Scheme 1, R = alkyl or aryl substituents) clearly suggests a measure of Lewis base character. Indeed, Kuhn has employed 1,3,4,5-tetramethyl-2-methyleneimidazoline as a donor ligand to bind transition-metal and main-group Lewis acidic species.[16]

Scheme 1. Resonance Forms of N-Heterocyclic Olefins



Scheme 2. Syntheses of NHO 1



The sterically demanding N-heterocyclic olefin NHC═CH_2 (**1**; NHC = $:C\{N(2,6\text{-}Pr^i_2C_6H_3)CH\}_2$) was synthesized by Rivard via reaction of the corresponding N-heterocyclic carbene with iodomethane (Scheme 2a; R = $2,6\text{-}Pr^i_2C_6H_3$).[17] This species, in turn, was utilized in the stabilization of low-oxidation-state main-group hydrides.[17] We recently reported the facile synthesis and molecular structure of the first anionic N-heterocyclic dicarbene (NHDC, $[:C\{[N(2,6\text{-}Pr^i_2C_6H_3)]_2CHCLi(THF)\}]_n$).[18] N-heterocyclic dicarbenes have been utilized in the preparation of NHDC−borane

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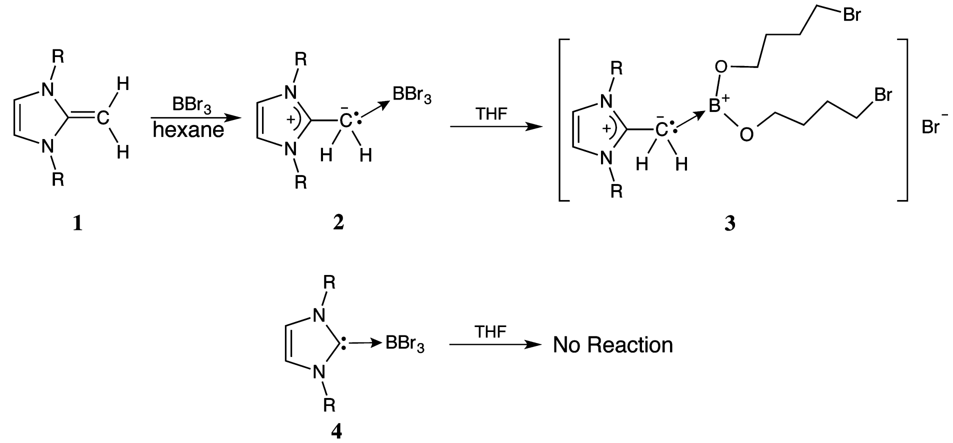
Scheme 3. Synthesis of Compounds 2 and 3



binuclear complexes,[19] "abnormal" carbene−borane complexes,[20] and NHC-stabilized triorganozincates.[21] Significantly, NHO (**1**) may facilely be prepared in high yield (86%) by reaction of the anionic NHDC with iodomethane (Scheme 2b; R = 2,6-$\mathrm{Pr}^i{}_2\mathrm{C}_6\mathrm{H}_3$).[22] Although the mechanism of formation of **1** remains obscure, it is plausible that lithium iodide elimination provides an open anionic C4 carbene site that may act as a suitably strong base to intermolecularly deprotonate the methyl cation that binds to the C2 carbene site of another imidazole ring, thereby giving **1** as the product.

While an NHO ligand has been utilized in binding group 13 cations $[\mathrm{GaX}_2]^+$ (X = Cl, Br, I),[23] the corresponding cationic chemistry of boron has not been explored. Herein, we report the syntheses, structures, and spectroscopic characterization of NHO-complexed BBr_3 (**2**) and borenium cation NHO:$[\mathrm{B}\{\mathrm{O}(\mathrm{CH}_2)_4\mathrm{Br}\}_2]^+$ ($\mathbf{3}^+$).[22] Notably, the borenium salt **3** is obtained by NHO:BBr_3 (**2**)-mediated ring opening of THF, thus presenting a new synthetic route to borenium cations.[2,3]

Compound **2** was synthesized in nearly quantitative yield (97%) by combining **1** with BBr_3 in hexane (Scheme 3; R = 2,6-$\mathrm{Pr}^i{}_2\mathrm{C}_6\mathrm{H}_3$). X-ray-quality crystals of **2** were subsequently obtained by recrystallizing **2** from either toluene or methylene chloride. It is well-known that, as a Lewis acid, BBr_3 may bind to the oxygen atom of an ether and then cleave a C−O bond of that ether.[24] However, without the ligand or substituent leaving from the boron center, Lewis base−BBr_3 adducts are usually not expected to exhibit this reactivity due to the coordinative and electronic saturation around the boron atom. Indeed, NHC−BBr_3 (**4** in Scheme 3; R = 2,6-$\mathrm{Pr}^i{}_2\mathrm{C}_6\mathrm{H}_3$), does not react with THF at ambient temperature. However, NHO−BBr_3 (**2**) is observed to slowly react with THF by cleaving the C−O bond of the latter and subsequently giving the corresponding borenium bromide salt $[\mathbf{3}^+]\mathbf{Br}^-$ in 64% yield (Scheme 3), thus clearly indicating that the reactivity of the Lewis acid core in these Lewis acid−Lewis base adducts may be dramatically affected by the electronic and steric properties of the Lewis base.

Compound **2** crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains two independent NHO−BBr_3 molecules (Figure 1; for clarity, only one NHO−BBr_3 molecule is shown) and one toluene solvent molecule.[22] In **2**, with donation of one pair of electrons of C(29) to the boron atom, the C(29)−C(30) bond is elongated from a C═C double bond in **1** (1.331(4) Å, average)[17] to a carbon−carbon single bond (1.497(14) Å). The B(2)−C(29) bond of 1.576(18) Å in **2** is about 0.05 Å shorter than that (1.623(7) Å) in **4**,[25] which may be due to the steric effect of **1** being less than that of the corresponding NHC (NHC = :C{N(2,6-$\mathrm{Pr}^i{}_2\mathrm{C}_6\mathrm{H}_3$)CH}$_2$) ligand.[26] As in compound **4**, the boron atom in **2** is also four-coordinate and adopts a tetrahedral geometry. However, the ^{11}B NMR resonance[22] (−10.29 ppm) of **2** shifts downfield in comparison with that (−16.46 ppm) of **4**,[25] indicating the relatively weak electron-donating ability of the NHO ligand **1**.

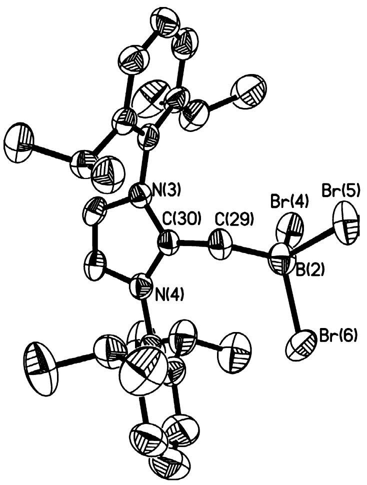


Figure 1. Molecular structure of NHO−BBr_3 (**2**). Thermal ellipsoids represent 30% probability; hydrogen atoms on carbon are omitted for clarity. Selected bond distances (Å) and angles (deg): B(2)−C(29) = 1.576(18), B(2)−Br(4) = 2.037(15), B(2)−Br(5) = 2.034(14), B(2)−Br(6) = 2.042(15), C(29)−C(30) = 1.497(14); B(2)−C(29)−C(30) = 121.3(9), C(29)−B(2)−Br(4) = 112.9(9), C(29)−B(2)−Br(5) = 107.6(8), C(29)−B(2)−Br(6) = 115.2(9).

Borenium cation $\mathbf{3}^+$ (Figure 2) contains a three-coordinate boron in a trigonal-planar geometry (the sum of the bond angles around the B(1) atom is 360°). The 3.92 Å distance between the cationic boron center and the counteranion Br^- is larger than the sum of van der Waals radii of B and Br (3.77 Å), ruling out the presence of real close contacts between them.[27] The B−C bond in $\mathbf{3}^+$ (1.530(13) Å) is shorter than that in **2** (1.576(18) Å), which indicates the relatively strong donor−acceptor interaction between the NHO ligand **1** and the electron-deficient cationic boron center. It is also noteworthy that the reported B−$\mathrm{C}_{\mathrm{NHC}}$ bond distances of NHC-stabilized borenium cations are in the range 1.58−1.60 Å.[4,8,11,13,14] While these compare well to those in an NHC-stabilized dihydrox-

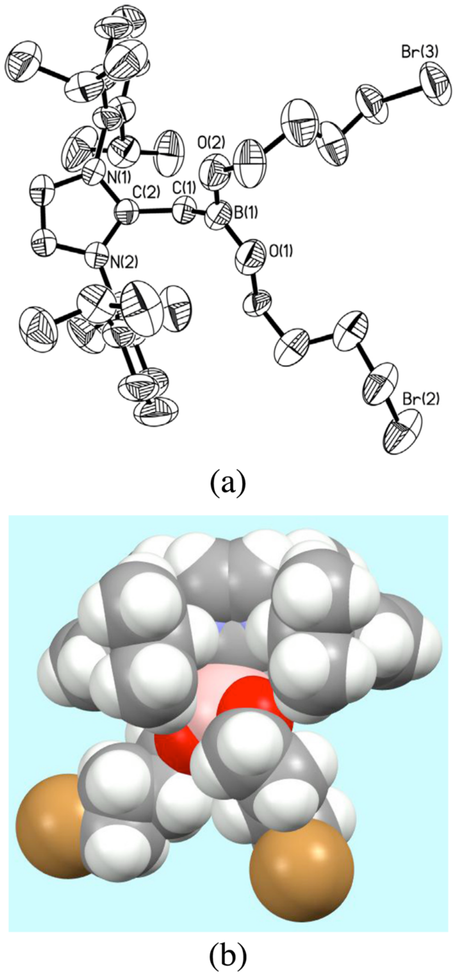


Figure 2. (a) Molecular structure of the borenium cation 3^+. Thermal ellipsoids represent 30% probability; hydrogen atoms on carbon are omitted for clarity. Selected bond distances (Å) and angles (deg): B(1)−C(1) = 1.530(13), B(1)−O(1) = 1.345(11), B(1)−O(2) = 1.339(11), C(1)−C(2) = 1.472(9); B(1)−C(1)−C(2) = 119.5(7), C(1)−B(1)−O(1) = 127.9(9), C(1)−B(1)−O(2) = 114.6(9), O(1)−B(1)−O(2) = 117.5(9). (b) Space-filling model of 3^+ (B, pink; O, red; Br, brass; C, gray; N, blue; H, white).

yborenium cation (1.310 and 1.307 Å),[8] the B−O bonds in $\mathbf{3}^+$ (1.345(11) and 1.339(11) Å) reside between the B−O single bond (1.663 Å) in an abnormal NHC-stabilized $B(Et)_2OTf$[20] and the B═O double bond (1.304 Å) in a Lewis acid coordinated oxoborane.[28] This suggests that an electron lone pair on each oxygen in $\mathbf{3}^+$ may engage in π donation to the vacant p orbital of the central cationic boron atom. Both the O-to-B π donation and the pronounced steric shielding (as shown in Figure 2b) of the NHO ligand and two $O(CH_2)_4Br$ chains favor the stability of $\mathbf{3}^+$. The cationic character of $\mathbf{3}^+$ is further endorsed by the obviously downfield ^{11}B NMR chemical shift (+26.60 ppm) in comparison to that (−10.29 ppm) of the precursor **2**. Moreover, the ^{11}B NMR chemical shift (+26.60 ppm) of $\mathbf{3}^+$ compares well to that (+22.5 ppm) of the dihydroxyborenium cation $[NHC{:}B(OH)_2]^+$ (NHC = :C{N-(2,6-$Pr^i_2C_6H_3$)CH}$_2$).[8]

In conclusion, we report a new anionic-NHDC-based synthetic strategy for the preparation of ylidic N-heterocyclic olefins (NHOs) (**1**). Utilizing this platform, we report the synthesis and characterization of the first NHO-stabilized boron tribromide (**2**) and borenium cation ($\mathbf{3}^+$). The cation $\mathbf{3}^+$ is obtained by NHO−BBr_3 (**2**)-mediated ring opening of THF, representing a unique synthetic method to access borenium cations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving full details of the syntheses and X-ray crystal determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(22) See the Supporting Information for synthetic and crystallographic details.

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