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Superelectrophilicity of 1,2-Azaborine: Formation of Xenon and Carbon Monoxide Adducts

Klara Edel,

Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen (Germany)

Jacob S. A. Ishibashi,

Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467-3860 (USA)

Shih-Yuan Liu, and

Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467-3860 (USA)

Holger F. Bettinger*

Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen (Germany)

Abstract

The BN analogue of *ortho*-benzyne, 1,2-azaborine, is shown to bind carbon monoxide and a xenon atom under matrix isolation conditions, demonstrating its strongly Lewis acidic superelectrophilic nature. The Lewis acid–base complexes involving CO and Xe can be cleaved photochemically and reformed by mildly annealing the matrices. The interaction energy of 1,2-azaborine with Xe is 3 kcal mol^{−1} according to quantum chemical computations, and is similar to that of the superelectrophilic carbene difluorovinylidene.

Keywords

1,2-azaborine; carbon monoxide; Lewis acids; matrix isolation; xenon

Azaborine **1** is the formal analogue of 1,2-didehydrobenzene (*ortho*-benzyne) **2**, as the C1–C2 linkage is replaced by the isoelectronic BN unit (see Scheme 1).^[1] After the report of the first successful self-trapping of a 1,2-azaborine derivative,^[2] the parent **1** could be isolated in solid argon and characterized by direct spectroscopic techniques.^[3] It was found to readily react with the small molecules dinitrogen and carbon dioxide under cryogenic matrix isolation conditions. Similar reactivity was recently established for borylenes under matrix isolation and conventional conditions.^[4] Although the reactivity of **2** is high, allowing diverse chemical transformation with high potential for organic chemistry,^[5] it is

* holger.bettinger@uni-tuebingen.de.

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Conflict of interest

The authors declare no conflict of interest.

not known to react with these rather inert molecules under similar conditions. The BN-heterocycle **1** thus represents a novel class of reactive intermediate that unites the properties of an electrophilic boron and a nucleophilic nitrogen center providing the means for high reactivity and significant potential in synthesis.

The properties of **1** revealed so far indicate that the boron center is highly electrophilic. This is in line with computations that show that the lowest-energy unoccupied molecular orbital (LUMO) is predominately centered on boron and lies within the molecular plane, while the HOMO–1 is located on the nitrogen atom (see Scheme 1).^[3a,6] The Wiberg bond index points towards a double, rather than a triple bond that would be expected based on the isoelectronic relationship to **2**.^[3a] This could make **1** chemically more similar to a putative “2-borapyridine” than to *ortho*-benzynes. The closely related borabenzene (borine) is unknown in free form, but its dinitrogen adduct has been characterized.^[7] In our ongoing studies of the chemical behavior of **1**, we have studied its reactivity towards additional Lewis bases of varying basicity. We here report the interaction of **1** with carbon monoxide and xenon. Carbon monoxide was chosen because it is a stronger Lewis base than dinitrogen, but also has the potential to undergo cycloaddition reactions with **1**. Xenon, on the other hand, is a very weak Lewis base that interacts only with very strong electrophiles, for example, the superelectrophilic difluorovinylidene.^[8] The possibility of a bonding boron–xenon interaction has been probed computationally,^[9] but experimental evidence for the B–Xe interaction is very rare and mostly limited to mass spectrometry investigations.^[10] We here show that the boron center in **1** acts as a Lewis acid towards CO (Lewis acid–base vs. [2+1] or [2+2] cycloaddition) and Xe, providing the first example of a boron–xenon interaction probed by direct spectroscopic techniques.

The trapping of **1** with CO was achieved by condensing the products of flash vacuum thermolysis (FVT) of precursor **3** with a mixture of Ar and CO in various ratios (Scheme 2, Figure 1). In separate experiments, the isotopologues ¹³CO and C¹⁸O were employed in order to obtain isotopic shifts of vibrational bands for comparison with computations.

The infrared spectrum obtained after co-condensation of **1** and 10 % CO in argon at 8 K allows identification of a distinct set of bands that decrease in intensity upon irradiation with light of wavelength $\lambda > 395$ nm, while the bands of **1** form concomitantly (Figure 1a). Subsequent annealing of the matrix to 12 K results in decrease of the bands of **1** and increase of the original bands (Figure 1b). These we ascribe to result from the Lewis acid–base complex **4** between **1** and CO that is C-terminally bound based on the comparison with the vibrational spectrum computed at the CCSD(T)/TZ2P level of theory (Figure 2).

The CO stretching frequency of **4** is almost hidden by that of free CO, which is present in a large excess, but can be revealed in the difference spectra obtained after 395-nm-irradiation (see Figure S1). It is observable at 2134 cm^{–1} for **4** with natural isotope composition of CO and at 2086 cm^{–1} and 2088 cm^{–1} for the ¹³CO and C¹⁸O isotopologues, respectively (see Figure S2). These isotopic shifts of 48 cm^{–1} (¹³C¹⁶O vs. ¹²C¹⁶O) and 46 cm^{–1} (¹²C¹⁸O vs. ¹²C¹⁶O) are in very good agreement with those computed for **4** (50.4 cm^{–1} and 48.2 cm^{–1}, respectively, see Table S1).

In addition to the signals of **4**, a band at 1860 cm^{-1} with isotopic shifts of 41 cm^{-1} (^{13}CO) and 45 cm^{-1} (C^{18}O) could be observed when the gaseous species were frozen in a matrix at 8 K. On the other hand, if the temperature of the cold spectroscopic window was warmed to 30 K during deposition, this band was not observed. This indicates that this band is due to a thermally labile product. Its vibrational transition at 1860 cm^{-1} suggests the presence of a carbonyl group in a small strained ring. For example, the $\nu(\text{CO})$ stretching vibration of benzocyclopropenone^[11] was reported at 1869 cm^{-1} (a slightly lower energy band at 1838 cm^{-1} was assigned to this vibration in earlier work).^[12] Hence, the BN-benzocyclopropenone **5** is a reasonable candidate for the 1860 cm^{-1} band. We were not able to obtain **5** as stationary point at various levels of theory (B3LYP, MP2, and CCSD(T)) as attempted optimizations resulted in **4** instead. Only if the effect of solvent (we chose the polar water) was taken into account in the form of a polarizable continuum at the B3LYP/6-311 + G** level of theory, **5** is obtained as minimum. At this level of theory, the $\nu(\text{CO})$ stretching vibration is computed to be 1877 cm^{-1} while ring opening to **4** has a classical barrier lower than 0.1 kcalmol^{-1} and is exothermic by 22 kcalmol^{-1} . Based on these computational results, it is tentatively suggested that the band at 1860 cm^{-1} is due to **5**. The bicyclic carbene **6** that would result from a formal [2+2] cycloaddition reaction between **1** and CO is a high-energy isomer of **4** ($+35\text{ kcalmol}^{-1}$ in its singlet state; the singlet–triplet energy splitting is 37 kcalmol^{-1} in favor of the singlet state). We have no experimental evidence for formation of **6**, but note that it lacks characteristic strong infrared bands (see Table S2).

The trapping of **1** with CO demonstrates that Lewis acid–base interaction is significantly preferred over [2+1] or [2+2] cycloaddition reactions. This behavior prompted the investigation of **1** towards significantly weaker Lewis bases than CO or N_2 , and we chose Xe as this most reactive noble gas is known to interact with superelectrophilic carbenes^[8,13] and the *closo*-dodecaborate anion $[\text{B}_{12}\text{Cl}_{11}]^-$.^[10c] Trapping the products of FVT of **3** in mixtures of argon and xenon results in a new set of signals that decrease in intensity upon irradiation ($\lambda > 320\text{ nm}$), while those of **1** form (Figure 3a). Subsequent annealing of the matrix to 12 K causes a decrease of the signals of **1** and regrowth of those associated with the novel compound (Figure 3b).

We assign this to a Lewis acid–base complex of **1** with Xe (**7**) based on the comparison with the IR spectrum computed at the B3LYP-D3(BJ)/cc-pVTZ(-PP) level of theory (Figure 4, see Table S3 for harmonic vibrational frequencies and anharmonic corrections).^[14] The B–Xe stretching vibration is computed at 49 cm^{-1} and thus not observed by IR spectroscopy. The experiment shows that not only CO and N_2 interact with **1**, but also the significantly weaker Lewis base Xe, thereby revealing the superelectrophilic nature of this novel reactive intermediate.

In order to compare the B–Xe interaction in **7** with data reported for the *closo*- $[\text{B}_{12}\text{Cl}_{11}]^-$ –Xe adduct, we have performed computations using Møller–Plesset perturbation theory to second order (MP2) (see the Supporting Information for details). Note that B3LYP-D3(BJ) gives similar binding energies (see the Supporting Information). The computed bond dissociation energies of **1**·X increase from Xe over N_2 to CO as expected (Table 1). Comparison with binding energies for the *closo*- $[\text{B}_{12}\text{Cl}_{11}]^-$ anion shows that the interaction

of **1** with these small molecules is significantly weaker.^[10c] The binding energy of **1**·Xe, on the other hand, is similar to that reported for the difluorovinylidene–Xe complex F₂CC·Xe.^[8]

The boron–xenon distance of 2.87 Å in **1**·Xe is significantly longer than the C–Xe distance of F₂CC·Xe (2.38 c) and the B–Xe distance of *closo*-[B₁₂Cl₁₁][−]·Xe (2.33 c).^[8,10c] As **1** may be considered a bora-pyridine, the comparison with the isoelectronic bora-benzene is instructive because a significantly larger interaction energy with Xe of 11 kcalmol^{−1} was predicted based on B3LYP computations earlier.^[9] Our computational analysis for the borabenzene–xenon complex arrived at a binding energy of 4.1 kcal mol^{−1} and a B–Xe distance of 2.60 Å, indicating that the adjacent nitrogen atom in **1** reduces the electrophilicity of boron compared to borabenzene. Finally, we note that besides the dative boron–xenon interactions described here and in the *closo*-[B₁₂Cl₁₁][−]·Xe adduct,^[10c] the synthesis of FXe–BF₂ with a covalent B–Xe bond was suggested.^[10a] Its B–Xe bond has a length of 2.21 Å according to our computations.

In summary, we have shown that the BN analogue of benzyne, BN-aryne **1**, has a superelectrophilic boron center as revealed by its attractive interaction with a xenon atom. In line with the character of the lowest unoccupied molecular orbital of **1**, which is boron centered and lies in the molecular plane, the boron center preferentially acts as a Lewis acid towards Lewis bases of variable strength (Xe, N₂, CO). The alternative reactivity by means of [2+1] or [2+2] cyclo-addition reactions is unimportant for CO, while a [2+2] cycloaddition is observed with CO₂.^[3a] Future research will probe the interactions of **1** with Lewis acids as well as its reactivity towards covalent bonds. It is expected that the polar nature of the BN unit will facilitate insertion into strong covalent polar bonds.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Difference spectra showing the reversible reaction $4 \rightleftharpoons 1 + \text{CO}$. a) IR difference spectrum obtained from the thermolysis products of **3** frozen at 8 K in a CO-doped (10 %) argon matrix after irradiation ($\lambda > 395 \text{ nm}$, 4 K, 30 min). The decreasing signals (pointing downwards) belong to carbon monoxide adduct **4**, increasing signals belong to **1** (blue stars). b) Difference spectrum after subsequent annealing for 10 minutes at 12 K (starting from 4 K) showing reversibility of the reaction $4 \rightleftharpoons 1 + \text{CO}$. c) IR spectrum of **1** computed at the CCSD(T)/ TZ2P level of theory.^[3a]

Figure 2.

a) Computed IR spectrum of **1** at the CCSD(T)/TZ2P level of theory.^[3a] b) IR difference spectrum obtained from the thermolysis products of **3** frozen at 8K in an argon matrix doped with 10 % CO after irradiation ($\lambda > 395$ nm, 4 K, 30 min). c) IR spectrum of **4** computed at the CCSD(T)/TZ2P level of theory.

Figure 3.

Difference spectra showing the reversible reaction $7 \rightleftharpoons 1 + \text{Xe}$. a) IR difference spectrum obtained from the thermolysis products of **3** frozen at 8K in Ar/Xe (60:40) after irradiation ($\lambda > 320 \text{ nm}$, 4 K, 35 min). The decreasing signals (pointing downwards) belong to xenon adduct **7**, increasing signals belong to **1** (blue stars). b) Difference spectrum after subsequent annealing for 18 minutes at 12 K (starting from 4 K) showing reversibility of the reaction $7 \rightleftharpoons 1 + \text{Xe}$. c) IR spectrum of **1** computed at the CCSD(T)/TZ2P level of theory.

Figure 4.

a) IR difference spectrum obtained from the thermolysis products of **3** frozen at 8K in Ar/Xe (60:40) after irradiation ($\lambda > 320$ nm, 4 K, 35 min). b) IR spectrum of **7** computed at the B3LYP-D3(BJ)/cc-pVTZ(-PP) level of theory.

Scheme 1.

Two resonance forms of 1,2-azaborine (**1**) demonstrating the isoelectronic relationship to 1,2-didehydrobenzene (*ortho*-benzyne, **2**) and the LUMO and HOMO-1 of **1** (left).

Scheme 2.

Flash vacuum thermolysis (FVT) of **3** and trapping in CO- or Xe-doped argon matrices results in **4** and **7**, respectively, which can undergo reversible photochemical cleavage. A band observed at 1860 cm^{-1} is tentatively assigned to compound **5**, while no evidence for formation of **6** was obtained.

Table 1:

Bond dissociation energies (in kcalmol⁻¹) corrected for zero-point vibrational energies for Lewis acid–base complexes of **1**·X computed at the MP2/cc-pVTZ(-PP) level of theory unless noted otherwise.

X	Xe	N₂	CO
1	2.8	10.1	28.0
[B ₁₂ Cl ₁₁] ^[a]	26	43	71

^[a]MP2/6-311 + + G(2d,2p)/SDD data without ZPVE correction taken from Rohdenburg et al.^[10c] and converted to kcalmol⁻¹.