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C-H Bond Amination by Photochemically Generated Transient BoryInitrenes at Room Temperature: A Combined Experimental and Theoretical Investigation of the Insertion Mechanism and Influence of Substituents

Matthias Filthaus,^{†,‡} Larissa Schwertmann,[‡] Patrik Neuhaus,[‡] Rüdiger W. Seidel,[§] Iris M. Oppel,^{||} and Holger F. Bettinger^{*,†,‡}

[†]Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany [‡]Lehrstuhl für Organische Chemie II and [§]Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany

Institut für Anorganische Chemie, RWTH Aachen, Landoltweg 1, 52074 Aachen, Germany

Supporting Information

ABSTRACT: A number of azidoboranes having substitution patterns that are derived from catechol (3), pinacol (4a), 1,2-diaminoethane (4b,c), 1,2-ethanedithiol (4d), and 1,2,4,5-tetrahydroxybenzene as well as acyclic dialkoxy species (5) were synthesized and, in the case of 4c (N,N'-ditosyl-2-azido-1,3,2-diazaborolane), also structurally characterized. The azidoboranes were photolyzed in cyclohexane solvent



in order to investigate the tendency of the generated borylnitrenes to undergo intermolecular C–H insertion reactions. The yields of intermolecular insertion products ranged from very good (4a) to vanishingly small, depending on the substitution of the azidoborane. For a number of borylnitrenes the zero-field splitting parameter *D* was measured in organic glasses at 4 K. The small primary kinetic isotope effect ($k_{\rm H}/k_{\rm D} = 1.35$) measured for 4a in mixtures of [H_{12}]cyclohexane and [D_{12}]cyclohexane suggests that the insertion reaction is concerted and involves the singlet state of the borylnitrene. Computations at the CBS-QB3 and CCSD(T)/TZ2P levels of theory show that the relative energies of singlet and triplet states of a wide variety of borylnitrenes and even their nature as minima or saddle points depend strongly on the substituents. Photolysis of the most reactive azidoborane, 4a, in methane in a flow reactor at atmospheric pressure produces an intermolecular insertion product in low yields, in agreement with the expectation of intersystem crossing to the less reactive triplet state of the borylnitrene.

INTRODUCTION

Borylnitrenes 1 are related to vinylidenes 2 due to substitution of the CC group by the isoelectronic BN unit (Chart 1).¹ While





the parent vinylidene **2a** is a transient reactive intermediate,^{2–12} the difluoro derivative **2b** can be generated photochemically from difluoroethyne and observed directly by spectroscopy using matrix isolation techniques. Under matrix isolation conditions high reactivity is observed for **2b** upon annealing toward a variety of substrates, including CH_4 , H_2 , and Xe.^{13–18} Therefore, **2b** was termed "superelectrophilic" by Sander et al.¹⁹

In our previous work we demonstrated that oxygensubstituted borylnitrene 1a, photochemically accessible from the corresponding azide 3a, is also highly reactive under matrix isolation conditions.^{1,20–23} In contrast to 2b, however, 1a requires photochemical excitation using visible light to undergo insertion reactions into CH_4 or H_2 if isolated in solid argon.^{21,22} Further investigations in solution at room temperature revealed that the pinacol derivative 1b is a ferocious intermediate that inserts into the C–H bonds of hydrocarbon solvents very efficiently without selectivity after statistical correction.²¹

While the intramolecular C–H insertion of transient nitrenes is a well-known reaction,^{24–28} efficient intermolecular C–H insertion reactions are limited to highly electrophilic nitrenes. Examples are fluorinated phenyl (R = C₆H_nF_{5–n})-,^{29–34} cyano (R = NC)-,³⁵ carbonyl (R = R'CO)-,^{36,37} and oxycarbonylnitrenes (R = R'OCON),^{38–47} as well as the "inorganic" sulfonyl (R = R'S(O)₂)-^{48,49} and phosphorylnitrenes (R = (R'O)₂P-(O)).^{50,51} Furthermore, transition-metal-mediated amination or amidation of C–H bonds is currently receiving significant attention.^{52–62}

Received: January 26, 2012 Published: May 3, 2012 Scheme 1. Synthesis of the Azidoboranes 3-6 Investigated in the Present Work from the Corresponding Chloroboranes 7-10



Prior to our work, Paetzold and co-workers have shown that thermolysis and photolysis of azidoboranes generally results in iminoboranes RBNR without the involvement of transient borylnitrenes. $^{63-67}$ It was possible to trap borylnitrenes in intramolecular and intermolecular reactions only in the case of the thermolysis (gas phase) or photolysis (cyclohexane solution) of diaminoazidoboranes (R2N)2BN3 with bulky substituents (R = *i*-Pr, 2,6-dimethylpiperidino).⁶⁶ Efficient insertion into the C-H bonds of solvent molecules was not observed by Paetzold and co-workers in their photolysis experiments with $(R_2N)_2BN_3$.⁶⁶ Rather, products isolated from the photolyses were explained to form by insertion of the borylnitrene $(R_2N)_2BN$ into one of the C-N (in the case of R = *i*-Pr) or B-NR₂ bonds (in the case of R = 2,6-piperidino) of an unreacted azide.⁶⁶ The nitrene that formed from this azide upon further irradiation then stabilized itself by intramolecular reactions with the bulky organic ligands via C-H insertion or hydrogen abstraction.

The factors that govern the reactivity of borylnitrenes in intermolecular C–H insertion reactions are uncertain at this time, as are mechanistic details. It is not understood why the nitrogen and oxygen derivatives investigated by Paetzold's group do not undergo intermolecular C–H insertion reactions. Is the high tendency toward intermolecular C–H insertion of **1b** due to the oxygen donor atoms or the chelate nature of the ligand, or are both essential? The limited knowledge of borylnitrene chemistry has prompted us to investigate the reactivity of borylnitrenes in more detail. The purpose of the present paper is to

- (i) evaluate the potential of various borylnitrenes in intermolecular amination reactions using cyclohexane as a model substrate
- (ii) deduce the spin multiplicity of the reactive intermediate by measurement of the primary kinetic isotope effects in cyclohexane solution
- (iii) demonstrate that the reactivity of 1b is sufficiently high to aminate methane in a flow reactor at room temperature and atmospheric pressure
- (iv) establish a theoretical basis for understanding borylnitrene properties with the help of computational chemistry techniques

RESULTS AND DISCUSSION

Synthesis of Azidoboranes. The azidoboranes 3-6 were synthesized from the corresponding known chloroboranes 7-10 by reaction with trimethylsilyl azide in dichloromethane solution (Scheme 1). All azides 3-6 are very moisture-sensitive, potentially explosive compounds.

Solid-State Structure of Compound 4c. Experimental structural data of azidoboranes with three-coordinate boron atoms are scarce.^{68–70} We therefore attempted to obtain single crystals of the new azidoboranes that are suitable for X-ray analysis, and we succeeded in the case of 4c. Single crystals of 4c were obtained by slow evaporation of the dichloromethane solvent. The compound crystallizes in the monoclinic space group C2. The molecule lies on a crystallographic 2-fold rotation axis, with the azide group being disordered by symmetry (Figure 1). The 1,3,2-diazaborolane framework is



Figure 1. Molecular structure of 4c. Symmetry-related atoms are denoted by "A".

essentially planar. The azido group is slightly bent $(N(2)-N(3)-N(4) = 168.6(12)^{\circ})$, as is typically observed for covalent azides. The B(1)-N(2)-N(3) angle is unusually large $(144.1(6)^{\circ})$ in comparison to those for related azides, presumably for steric reasons related to the bulky sulfonyl groups.

Solid-State Structures of PinBNH(cycloalkyl). We reported in our preliminary investigation of the photo-decomposition of **4a** in cycloalkane solvents high yields of C–H insertion products (see Scheme 2).²¹ The lability of the B–N bond of the aminoborane **11** under hydrolytic conditions

Scheme 2. Photochemical Reaction of 4a with Hydrocarbons and Products Obtained from Workup of Aminoborane 11



can be exploited for the transformation of (cyclo)alkanes into primary amines 12 or into amides 13 after acetylation of the aminoborane (Scheme 2).²¹

The aminoboranes obtained from reaction with cyclopentane (11b) and cyclohexane (11a) could be structurally characterized.²¹ The cycloheptane reaction product 11c could in the meantime also be crystallized, and the structure was solved (Figure 2).



Figure 2. Molecular structure of 11c.

Similarly to previously reported structures of pinBNH-(R),^{71,72} the crystal packing of all cycloalkyl derivatives features dimers that are bonded by two NH···O hydrogen bonds (Figure 3). The N···O distances increase from 3.13 to 3.23 Å



Figure 3. Hydrogen-bonded dimer of pinBN(H)cyclohexyl 11a and the intramolecular N···O distance in the crystal structure.

with increasing size of the alicyclic ring. The strength of the hydrogen bonds was computed at the SCS-RIMP2/def2-TZVP level of theory. According to these calculations, the dimer of 11a is more stable than the monomer by 9.7 kcal mol^{-1} .

Primary Kinetic Isotope Effect for CH Insertion of 1b. In principle, two fundamentally different mechanisms are conceivable for the amination of hydrocarbons by nitrenes (Scheme 3): abstraction of a hydrogen atom from the hydrocarbon substrate and rapid collapse of the resulting Scheme 3. Stepwise vs Concerted Mechanisms for the Insertion of Nitrene 1b into C–H Bonds



radical pair RP to the product (pathway A) or a one-step concerted insertion via transition structure TS into the C-H bond of the hydrocarbon substrate (pathway B).

One way of determining which of the two mechanisms is at work is the measurement of the kinetic isotope effect (KIE), $k_{\rm H}/k_{\rm D}$. A small KIE (1–2) is in agreement with a concerted reaction, while a large KIE is indicative of a hydrogen abstraction reaction. For example, the KIE for the C-H insertion of (diethoxyphosphoryl)nitrene was determined from reaction with mixtures of $[H_{12}]$ - and $[D_{12}]$ cyclohexane to be 1.02(3).⁵¹ This is clearly supportive of the involvement of a singlet nitrene. On the other hand, a large kinetic isotope effect $(k_{\rm H}/k_{\rm D}$ = 14.7(3)) was measured for the efficient intramolecular insertion of a photolytically generated (2-(2phenylethyl)phenyl)nitrene into a benzylic C-H bond, and it was concluded to involve the triplet state of the nitrene.^{73,74} We measured the isotope effect for the insertion reaction of 1b using mixtures of $[H_{12}]$ - and $[D_{12}]$ cyclohexane and arrived at a value of 1.35, indicative of a concerted insertion reaction involving the singlet state of 1b. Indeed, efficient intermolecular C-H insertion reactions are the hallmark of highly reactive singlet nitrenes.

Photogeneration of BoryInitrenes in Organic Glasses and ESR Spectral Properties of Triplet BoryInitenes. We measured the ESR spectra of the nitrenes generated photochemically from the azides 3a,b, 4a,c, and 6 in organic glasses at 4 K (Table 1). The |D/hc| values that were observed between 1.48 and 1.62 cm⁻¹ are typical for triplet nitrenes.⁷⁵ The |E/hc|values are 0 within the limited experimental accuracy of organic glasses for compounds 4c and 6. Wentrup and co-workers have established a linear correlation ($D = 1.96673\rho - 2.0577$ cm⁻¹)

Table 1. ESR Parameters (in cm⁻¹) Derived from Photolysis of the Corresponding Azides in Solid Methylcyclohexane (Unless Noted Otherwise) at 4 K and Values Computed from the Correlation of Wentrup et al.⁷⁵ Using the Spin Density ρ on N Determined at the UB3LYP/EPR-III Level of Theory

azide	lD/hcl	E/hc	D/hc (computed) ^b
3a	1.505	0.0038	1.456
3b	1.483	0.0027	1.429
4a	1.573	0.0047	1.626
4c	1.620 ^{<i>a</i>}	0	
6	1.602 ^{<i>a</i>}	0	

"Measured in 2-methyltetrahydrofuran. ^bUsing $D = 1.96673\rho - 2.0577 \text{ cm}^{-1}$.

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between the spin density ρ on the nitrogen center computed at the UB3LYP/EPR-III level and the *D* values deduced from the spectra, including borylnitrene **1a**.⁷⁵ We observe qualitative agreement between experiment and the correlation of Wentrup et al.⁷⁵ for compounds **3a**,**b** and **4a**, but we cannot compute the spin densities for the nitrene derived from **4c**, as the corresponding basis set for sulfur is not available. Due to the complicated electronic structure arising from the possible formation of two nitrene centers from **6**, UB3LYP computations were not performed for this system.

Photolysis of Azidoboranes 3–6 in Hydrocarbon Solvents. To evaluate the influence of the substituents at boron on the ability of borylnitrenes generated photolytically from azidoboranes to insert into unactivated C–H bonds of hydrocarbons, the following procedure was typically applied. The mixtures that were obtained from photolysis of azidoboranes in cyclohexane solution using a 254 nm light source were either reacted with alcohols (2-propanol or ethanol depending on the substituent at boron) or were treated with DMAP/AcCl followed by solid NaOH, as described previously (see Scheme 2).²¹ The solutions thus obtained were analyzed by GC-MS and GC after addition of external standards. In a few cases hydrocarbons other than cyclohexane were used.

We have demonstrated previously that the pinacol derivative **4a** inserts into a C–H bond of cyclohexane with a yield of 85%.²¹ To learn if the chelate nature of **4a** is essential for intermolecular C–H insertion, the acyclic derivative **5** was investigated. Photolysis indeed also produced cyclohexylamine after workup, but the yield was reduced considerably to 46%. As an additional product, the amino alcohol **14** was obtained in 15–20% yield (Scheme 4).





Formation of 14 is most readily explained by an intramolecular insertion into the β -C–H bond of the alkoxy substituent and cleavage of the resulting five-membered intermediate 15 by the alcohol. Insertion into an α -C–H bond would yield the four-membered ring 16, which should produce acetone and ammonia via hemiaminal 17 upon alcoholysis (Scheme 5). Despite careful searching, no products expected from α -C–H insertion could be detected. Also, the acetylation of primary photoproducts did not give any indication for α -C–H insertion. Formation of the less strained five-membered-ring species 15 is obviously favored.

The photolysis of $(CH_3O)_2BN_3$ in cyclohexane yields a colorless insoluble solid that can be degraded to hydrazine under basic conditions and to dinitrogen under acidic conditions according to Paetzold and Maier.⁶⁵ Thermolysis of $(CH_3O)_2BN_3$ in a closed tube, on the other hand, was reported to yield methoxyamine after saponification.⁶⁵ We were not able to detect any hydrazine derivatives or alkoxyamines from the photolysis of **5**.

We next consider azides of the chelate type with nitrogen or sulfur bound to boron: i.e., the 2-azido-1,3,2-diazaborolanes (**4b**,c) and 2-azido-1,3,2-dithiaborolane (**4d**). The gas-phase





thermolysis of **4b** at 500 °C was investigated previously by Paetzold et al.⁶⁶ In addition to unreacted **4b**, an HN₃ adduct of **4b** was identified as a reaction product.⁶⁶ Photolysis of **4b** produced a dark solution that was treated with 2-propanol. Among the many unidentified products, only trace amounts of cyclohexylamine, B(OiPr)₃, and bicyclohexyl were detected. The additional product with m/z 103 that can be detected by GC-MS may be due to amines **18–20**, which can form by intramolecular (**18** or **20**) or intermolecular (**19**) insertion reactions (Chart 2). Note that photolysis of diaminoazidobor-

Chart 2. Possible Amines 18-20 with m/z 103 Formed during Photolysis of 4b and Workup



anes $(R_2N)_2BN_3$ with bulky substituents yields dimers by insertion into the C–N or B–N bonds of an unreacted azide molecule according to Paetzold et al. (vide infra).⁶⁶

Neither 4c nor 4d is very soluble in cyclohexane. Photolysis of suspensions of 4c,d followed by alcoholysis with 2-propanol does not give any indication for intermolecular insertion into a solvent C–H bond.

We next consider azidoboranes 3 and 6 of the catechol type to investigate the influence of an aromatic ring on borylnitrene reactivity. Photolysis of the catechol derivative 3a under the conditions of matrix isolation (i.e., solid argon at 10 K) yields the corresponding nitrene 1a in its triplet ground state. This can photochemically react with methane by C-H insertion.²¹ In cyclohexane solution, on the other hand, no product of intermolecular C-H insertion could be identified. Irradiation of 3a in cyclohexane results in a yellow-brown solution and formation of a resin. Isolation of this resin indicates that it does not include any unreacted azide, as the typical azide band cannot be detected by IR spectroscopy. The resin is rather inert: treatment with alcohol, acid, or base at elevated temperatures or attempted acetylation did not give any indication for the formation of cyclohexylamine or amide. From the supernatant obtained after the photolysis a small amount of yellow solid could be isolated. Its alcoholysis or acetylation similarly did not produce any indication for the formation of functionalized cyclohexane. Compounds identified by GC-MS were B(OiPr)₃, 1,2-bis(acetyloxy)benzene, and bicyclohexyl, but acetamide or acetylated hydrazines were not

detected. Photolysis of the *tert*-butylcatechol derivative **3b** was similarly disappointing, as no indication for cyclohexane functionalization could be found. Running similar experiments in cyclooctane also produced negative results for **3a,b**.

As described above, formation of resins was observed earlier in the photochemistry of dialkoxyazidoboranes.⁶⁵ It is nonetheless puzzling that the photodecomposition of 3a does not produce cyclohexylamine derivatives. As the C-H insertion works even with CH₄ under cryogenic conditions, it may be speculated that the observations in solution are due to the instability of a possible aminoborane photoproduct under the reaction conditions. It is known that the expected primary photoproducts, CatBNHR (R = Me, Et, iPr), are oligomers (R = Me), dimers (R = Et), or mixtures of dimers and monomers (R = iPr).⁷⁶ Indeed, different properties of Bcat and Bpin have been noted and discussed previously.72,77,78 Attempts to investigate the photochemistry of independently synthesized CatBNHCy (Cy = cyclohexyl) failed, as we could not obtain the compound in a pure state from the reaction of CatBCl and cyclohexylamine in the presence of an amine base under a variety of experimental conditions.

Considering that detection of functionalized cyclohexane was not possible in the photochemistry of 3a,b in cyclohexane solution, it is surprising that the diazide 6 produces cyclohexylamine in 10-15% yield per azide group. Whether this result is due to the higher stability of the aminoborane expected to form by C-H insertion is unclear at this time.

Finally, we consider the photochemistry of **3c**. Due to its insolubility in cyclohexane the photodecomposition was performed in benzene. After alcoholysis or acetylation of the crude product mixture that contained insoluble resin-like materials, aniline or *N*-phenylacetamide was observed (GC-MS) in 11% or 15% yield. The mechanism of product formation is unclear, but Abramovitch et al.⁷⁹ concluded that arylnitrenes form adducts with benzene by interaction with its π system and that these adducts form aniline derivatives in dark reactions.³¹ Due to the low yield of C–H functionalized products, the reaction was not investigated further.

In summary, the pinacol system 4a is most efficient in the intermolecular insertion reaction into a C–H bond of cyclohexane solvent. The acyclic alkoxy compound 5 is less efficient, due to substantial intramolecular insertion reaction. While the nitrogen- and sulfur-substituted systems 4b-d as well as the aromatic compounds 3a,b give at most trace amounts of intermolecular insertion products, the diazide 6 performs better, for unknown reasons. Photodecomposition of 3c in benzene yields aniline, but the yield of functionalized benzene is lower than that observed for pentafluorophenylnitrene.³¹

Photolysis of 4a in Methane Gas at Room Temperature. The screening of a number of borylnitrenes toward the ability to insert into C–H bonds identified **1b** as the most efficient one. We were therefore intrigued by the question if C–H transformation of methane is possible with **1b** under conventional laboratory conditions, especially in view of the limited examples of nitrenes inserting into C–H bonds of methane.⁸⁰ Methane is a particularly challenging alkane to functionalize. The low reactivity of methane is reflected by its high first C–H bond dissociation energy (438.8 kJ/mol), high ionization potential (12.5 eV), low proton affinity (4.4 eV), low acidity (p $K_a = 48$), and a large HOMO–LUMO gap.^{81,82} The first step of any methane derivatization process requires the activation of an "inert" C–H bond. Highly reactive species as well as enzymatic systems can activate simple hydrocarbons, including methane.^{81–84} However, as the primary derivatization product generally has weaker C–H bonds than methane itself, a further complication lies in achieving the *selective* transformation of a single C–H bond of methane. Much success in methane transformation has been achieved in the field of transition-metal-mediated C–H functionalization chemistry over the years.^{56,85–90}

Bubbling dry methane through a pure sample of liquid **4a** at room temperature and atmospheric pressure yields a gas mixture that is passed through the quartz tube and continuously photolyzed using the output of the low-pressure mercury lamp (see Figure 4). Formation of a solid product from the gaseous



Figure 4. Schematic setup of the flow system used for the photolytic gas-phase transformation of methane into methylamine.

reactants is observed in the exposition zone and behind it during photolysis. Multinuclear NMR (¹H, ¹³C, and ¹¹B) investigations of the crude reaction products indicate the formation of the desired methane derivative PinBNHMe (11d) along with byproduct. The ¹¹B shift at 24.4 ppm is in the typical region of aminoboranes of type 11 and is in good agreement with our previous results for cycloalkane derivatization.²¹ The pinacol Me groups (δ (¹H) 1.22; δ (¹³C) 24.8) and NMe (δ (¹H) 2.51; $\delta(^{13}C)$ 23.3) are also observable by NMR of the crude products. The desired product 11d cannot be separated from the byproduct by crystallization or sublimation, due to its extreme air and moisture sensitivity. Nevertheless, the expected monomethylamine CH₃NH₂ can be detected by GC analyses after hydrolysis or alcoholysis with 2-propanol, along with ammonia (NH_3) and hydrazine (H_2NNH_2) . The photolysis reaction was also conducted under neat argon gas at room temperature. Under these reaction conditions no methylamine was detected after workup. Thus, the intramolecular rearrangement of a methyl group from the pinacol ligand to the nitrene center in 1b can be excluded as a possible source of methylamine.

Quantification of the reaction yield using GC-MS and GC on the basis of authentic samples could be achieved by acetylation of the crude aminoborane (Scheme 1). For this purpose the photolysis reaction was carried out until the azide 4a was completely consumed. The amount of unreacted azide 4a in the product mixture after photolysis could not be determined in our experiments, as it cannot be detected by GC due to decomposition. The reaction products were dissolved in diethyl ether and reacted with acetyl chloride (CH₃COCl) in the presence of N,N-dimethylaminopyridine (DMAP). The amount of derivatization product 13 ($R = CH_3$) was determined after addition of an internal standard by GC to be 6-8% based on consumed 4a, assuming quantitative acetylation. In addition, small amounts of AcNH₂ (via H abstraction) and the hydrazine derivatives AcNHNH₂ (via H abstraction/dimerization) were obtained.

On the basis of the KIE measurements in solution described above, it is expected that the singlet nitrene is responsible for the C-H insertion reaction also in the gas phase. The yield of C-H insertion product then depends decisively on the unknown lifetime of the singlet nitrene and the length of the mean free path. In the gas phase the mean free path is much longer than in the condensed phase, resulting in the "loss" of some singlet nitrene by formation of triplet nitrene. Indeed, the formation of AcNH₂ and AcNHNH₂ can be ascribed to the involvement of the triplet nitrene. In addition, the unknown quantum yield of the photochemical nitrene generation has a decisive influence on the overall reaction yield. It may be expected that reducing the mean free path by increasing the methane pressure will increase the yield further.

Theoretical Investigation of BoryInitrene Structures and Singlet-Triplet Energy Gaps. In order to better understand the properties of boryInitrenes and their involvement in the thermal or photochemical decomposition of azidoboranes, we investigated the influence of substituents on the boryInitrenes using computational chemistry techniques (see Tables 2–4 for energy data). We chose the complete basis

Table 2. Energy (in kcal mol⁻¹) of the Singlet States of X_2BN (¹A₁ in $C_{2\nu}$ and ¹A in C_1) and of XBNX Relative to the Lowest Energy Triplet State (³A₂) of X_2BN , As Computed at the CBS-QB3 Level of Theory^{*a*}

	Х				
	Н	CH ₃	NH ₂	OH	F
X_2BN , $C_{2\nu}$	-11.0 [1]	-2.9 [1]	+31.4 [3]	+27.2 [2]	+25.7 [0]
X_2BN , C_1	not exist.	not exist.	-0.4	+22.0	not exist.
$XBNX^{b}$	-89.0	-71.5	-2.1	+24.2	+47.0

^{*a*}A negative sign indicates that the singlet is lower in energy than the triplet state. The triplet X_2BN and singlet XBNX correspond to minima in all cases, while the $C_{2\nu}$ - X_2BN singlet can be a higher order stationary point, as given in brackets. ^{*b*}See also ref 130.

set extrapolation scheme CBS-QB3 of Petersson et al.^{91,92} This technique employs B3LYP geometry optimization and harmonic vibrational frequencies along with a number of

Table 4. Energy (in kcal mol⁻¹) of the Closed-Shell Singlet State of Unsaturated Cyclic Borylnitrenes and Their Corresponding Cyclic Iminoboranes Relative to the Lowest Energy Triplet State (${}^{3}A_{2}$) of the Respective Borylnitrene, As Computed at the CBS-QB3 Level of Theory^c

n =	1	2	3
	$-7.7 \ [0]^a$	-4.8 [1]	+13.3 [1]
	-14.0^{b}	-73.9^{d}	-38.1

^{*a*}Using int(grid=99590) in B3LYP geometry and vibrational frequency computation. The default integration grid results in Nimag = 1 (9*i* cm⁻¹). ^{*b*}Strongly distorted with a long N–C distance (1.782 Å); see also ref 132. ^{*c*}A negative sign indicates that the singlet is lower in energy than the triplet state. The triplet corresponds to a minimum in all cases, while the singlet can be a higher order stationary point, as given in brackets. ^{*d*}See also ref 133.

higher level single energy points up to the CCSD(T) level to extrapolate to a complete basis set estimate of the energy.

For the parent borylnitrene, H_2BN_1 , of $C_{2\nu}$ symmetry the open-shell configuration ... $(1b_1)^1(2b_2)^1$ can give rise to the ${}^{3}A_2$ and ${}^{1}A_{2}$ states, while the ... $(1b_{1})^{2}(2b_{2})^{0}$ configuration gives rise to the closed-shell ¹A₁ state. It was shown previously that the ${}^{1}A_{1}$ state is lower in energy than the ${}^{3}A_{2}$ and ${}^{1}A_{2}$ states.²⁰ However, the ¹A₁ singlet H₂BN corresponds to a first-order saddle point, and releasing the symmetry constraint during geometry optimization results in linear iminoborane, HBNH.^{20,93} A similar instability of singlet X₂BN toward rearrangement to XBNX is computed for $X = CH_3$. Thus singlet dialkylboryl nitrenes do not correspond to reactive intermediates and should not be observable directly or indirectly by trapping experiments. This conclusion is in agreement with observations made in the decomposition of dialkyl and diaryl boron azides, where borylnitrene-derived products have never been observed.

In contrast, the singlet diffuoro derivative F_2BN corresponds to a minimum in $C_{2\nu}$ symmetry and is thus stable with respect to rearrangement. The energetic ordering of singlet and triplet states changes by fluorine substitution: the triplet state is lower

Table 3. Energy (in kcal mol⁻¹) of the Closed-Shell Singlet State of Cyclic $C_2H_4X_2BN$, $C_2H_2X_2BN$, and Their Corresponding Cyclic Iminoboranes Relative to the Lowest Energy Triplet State (³A₂ Unless Noted Otherwise) of the Respective Borylnitrene, As Computed at the CBS-QB3 Level of Theory^{*a*}

X =	CH ₂	NH	0
	$-5.8[1]^{a}$	$+32.3 [1]^{a}$	+29.9 [0]
X		$+16.5 [0]^{b}$	
X`B " X´ ^N	-47.2 ^e	+23.8	not exist.
€ X́BN	-4.8 [1]	+24.8 [0] ^c	+33.7 [0]
X B N	-46.9	+37.1	not exist.

 ${}^{a}C_{2}$ symmetry for singlet and triplet (³A). ${}^{b}C_{1}$ symmetry for singlet. ${}^{c}C_{2}$ symmetry for singlet. ${}^{d}A$ negative sign indicates that the singlet is lower in energy than the triplet state. The triplet corresponds to a minimum in all cases, while the singlet can be a higher order stationary point, as given in brackets. ${}^{e}See$ also ref 131.

in energy than the singlet state, indicating that the fluorine atoms increase the electron density in the boron p orbital. While the rearrangement from X_2BN to XBNX is a highly exothermic process for X = H, CH_{3} , it is endothermic for X = F (Table 2).

Of particular interest are the diamino and dihydroxy borylnitrenes. Their $C_{2\nu}$ -symmetric structures are higher order stationary points on the singlet state potential energy surface. The presence of donor groups (OH, NH₂, as well as F discussed above) destabilizes these singlet states such that the triplet nitrenes are significantly lower in energy. As discussed previously in the context of 3a,²⁰ donors increase the electron density in the boron π orbital and thus reduce its Lewis acidity and its ability to accept π electrons from nitrogen. This results in a destabilization of the singlet relative to the triplet state. Relaxing the symmetry constraint results in asymmetric structures of the singlet nitrenes with one "bridging" XH (X = O, NH) group (Figure 5).



Figure 5. Structures of $(HO)_2BN$, $(H_2N)_2BN$, and $C_2H_4(NH)_2BN$ as computed at the B3LYP/6-311G(2d,d,p) and CCSD(T)/TZ2P (in italics) levels of theory. Distances between non-hydrogen atoms are given in Å; the angles are given in degrees.

As the CBS-QB3 model relies on B3LYP geometries, we also performed CCSD(T)/TZ2P geometry optimizations to confirm the existence of these stationary points on the PES. The structure of (HO)₂BN is characterized by a small O2-B-N angle (79.1°) and a short distance (1.800 Å) between O2 and N1. In $(H_2N)_2BN$, the corresponding angle and distance are even smaller (68.1° and 1.614 Å). The structures of these borylnitrenes are reminiscent of that reported for formylnitrene, HC(O)N, which is intermediate between nitrene and oxazirene.⁹⁴⁻⁹⁶ The dative in-plane interaction between an oxygen lone pair and a vacant orbital at nitrogen provides the driving force for the distortion of formylnitrene and the stabilization of the singlet relative to the triplet state.94-96 Likewise, the distortion of (HO)₂BN and (H₂N)₂BN are indicative of dative interactions between the boron-bound donor groups and the nitrene nitrogen atom. These interactions are stabilizing the singlet relative to the triplet state. While the triplet remains the ground state for $(HO)_2BN$, the singlet and triplet states are almost isoenergetic for $(H_2N)_2BN$ (Table 2).

The existence of these distorted borylnitrenes as minima on the potential energy surface should make singlet $(HO)_2BN$ and $(H_2N)_2BN$ in principle observable. Their rearrangements to the iminoboranes are close to thermoneutral, making the trapping of the borylnitrene competitive. The results of the computations are in agreement with the report by Paetzold et al.⁶⁶ for photochemical decomposition of $(R_2N)_2BN_3$, iminoborane formation in case of $(CH_3O)_2BN_3$ thermolysis, and with our results for **Sa,b** described above. Carbocyclic singlet borylnitrenes do not correspond to minima (see Tables 3 and 4), similar to acyclic $(CH_3)_2BN$. They should thus not be trappable and transform to the corresponding cyclic iminoboranes, in agreement with the observations of Paetzold and co-workers.⁹⁷ An exception is the *B*-nitrenoborirene (Table 4). This has a singlet ground state, and its rearrangement is only mildly exothermic. These properties would make it a particularly attractive borylnitrene for C–H insertion. Its synthesis, however, may be challenging. The oxygen- or nitrogen-containing heterocyclic singlet

borylnitrenes are minima (Table 3). The 2-nitreno-1,3,2diazaborolane is exceptional: similar to the case for the acyclic $(H_2N)_2BN$ it prefers a distorted structure with an intramolecular stabilization of the nitrene center by one of the nitrogen lone pairs (see Figure 5). Geometry optimization at the CCSD(T)/TZ2P level of theory confirms the existence of this minimum on the PES. The corresponding iminoboranes do not exist as stationary points on the potential energy surface in case of X = O, while their formation from the borylnitrene is endothermic for X = NH. The triplet states, however, are lower in energy than the singlets and therefore intersystem crossing is in principle a reaction channel that can compete with singlet insertion reactions.

CONCLUSIONS

The combined experimental and computational investigation of azidoborane photolysis in (cyclo)alkanes allows drawing the following conclusions.

- 1. The small kinetic isotope effect measured for the efficient intermolecular insertion of borylnitrene **1b** into a C–H bond of cyclohexane is in agreement with a concerted reaction involving the singlet state of the nitrene.
- 2. The substituents at the boron atoms have a significant influence on the intermolecular C-H insertion chemistry. The pinacolato group is the most efficient and results in efficient C-H insertion. This chelate precludes the intramolecular C-H insertion that is an important side reaction in the closely related acyclic dialkoxy derivative. No or at most low yields of intermolecular C-H insertion products are obtained for the cyclic aza (4b,c) or thia (4d) as well as for the catecholato derivatives (3). In particular, the failure of this last class of borylnitrenes to efficiently produce C-H insertion products in solution is surprising in view of the behavior observed for 3a earlier in matrix isolation studies. On the other hand, the 1,2,4,5-tetrahydroxybenzene-derived diazide 6 yields intermolecular C-H insertion products in modest yields.
- 3. The computations for acyclic and cyclic carbon substituted singlet borylnitrenes show that these, with the exception of experimentally unknown nitrenoborirene, do not correspond to minima, in agreement with numerous experimental studies. Heteroatom substitution (NR₂, OR, F) turns the singlet borylnitrenes into minima and thus in principle they are experimentally observable, in agreement with previous trapping and matrix isolation studies. However, triplet states are lower than or very close in energy to the singlet states and thus triplet state chemistry, as well as rearrangement to acyclic iminoboranes, may compete with C–H insertion of the singlet state.

4. The observations under matrix isolation conditions and in solution and the possible unproductive escape of the singlet borylnitrene to the triplet state have prompted us to investigate the reaction in the gas phase. Photolysis of a mixture of azidoborane 4a and methane in a flow reactor under atmospheric pressure results in a 6–8% yield of intermolecular C–H insertion based on consumed 4a. While this yield is low, the observation of intermolecular C–H insertion products at all demonstrates the high reactivity of 1b.

EXPERIMENTAL AND THEORETICAL SECTION

General Considerations. All manipulations were carried out under a dry argon atmosphere in oven-dried Schlenk type glassware or in a glovebox. Solvents and substrates were dried before use (cycloalkanes, Na; CH_2Cl_2 , CaH_2) and stored over activated molecular sieves (3 Å). The chloroboranes 7b, ^{98,99} 7c, ¹⁰⁰ 8b, ¹⁰¹⁻¹⁰³ 8c, ^{104,105} 8d, ¹⁰⁶⁻¹⁰⁸ 9a,b, ^{109,110} and 10¹¹¹ and the azides 3a, ⁶⁸ 4a, ²¹ and 4b⁶⁶ were prepared according to the literature. 1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DRX 200 and ¹¹B NMR spectra on a Bruker DPX 250 spectrometer. ¹H (200 MHz) and ¹³C (50 MHz) chemical shifts are relative to tetramethylsilane, and ¹¹B (80 MHz) chemical shifts are relative to BF3 OEt2. GC/MS analyses used helium gas and a Zebron ZB-5mS (Phenomenex) capillary column (length 30 m, i.d. 0.25 mm, film thickness 0.25 μ m). GC analyses used hydrogen gas and a CP-Wax 51 Amin FS (Varian) capillary column (length 25 m, i.d. 0.32 mm, film thickness 1.20 μ m). The yields of the products determined by GC are based on cycloheptylamine as an internal standard and are response-corrected on the basis of authentic samples where available. IR spectra were measured on a Bruker Equinox 55 spectrometer. EPR spectra were recorded on a Bruker Elexsys E500 spectrometer. The computer simulations of the EPR spectra were performed by using the XSophe computer simulation software suite (version 1.0.4),¹¹² developed by the Centre for Magnetic Resonance and Department of Mathematics, University of Queensland, Brisbane, Australia, and Bruker Analytik GmbH, Rheinstetten, Germany. Irradiations were carried out with a Gräntzel low-pressure mercury lamp (254 nm).

General Procedure for Synthesis of Azides. To a solution of the chloroborane in dichloromethane (20 mL per 1 g of chloroborane) was added trimethylsilyl azide (1.0-1.5 equiv) at -80 °C. After slow warming to room temperature overnight, the volatiles were removed under reduced pressure. The azides were purified by recrystallization or condensation and stored under argon in a refrigerator.

3b: recrystallization from hexane; yield 2.18 g (77%). ¹H NMR (CD_2Cl_2) : δ 1.4 (s, 9 H, $C(CH_3)_3$), 7.1–7.3 (m, 3 H, ArH). ¹³C{¹H} NMR (CD_2Cl_2) : δ 31.7 $(ArC(CH_3)_3)$, 35.1 $(ArC(CH_3)_3)$, 109.9 (ArC), 111.8 (ArC), 120.0 (ArC), 145.7 $(CC(CH_3)_3)$, 147.2 $(ArCOBN_3)$), 147.9 $(ArCOBN_3)$. ¹¹B{¹H} NMR (CD_2Cl_2) : δ 26.2. IR (NaBr): 2160 cm⁻¹.

3c: product washed with pentane; yield 1.33 g (90%). ¹H NMR (CD₂Cl₂): δ 7.38 ppm (m, 2 H, ArH), 7.49 (s, 2 H, ArH), 7.75 (m, 2 H, ArH). ¹³C{¹H} NMR (CD₂Cl₂): δ 108.9 (ArC), 125.4 (ArC), 127.8 (ArC), 130.4 (ArC), 147.4 (ArCOBN₃). ¹¹B{¹H} NMR (CD₂Cl₂): δ 25.2.

4c: recrystallization from dichloromethane; yield 5.78 g (76%). ¹H NMR (CD₂Cl₂): δ 2.44 (s, 6 H, ArCH₃), 3.54 (s, 4 H, CH₂), 7.37 (m, 4 H, ArH), 7.75 (m, 4 H, ArH). ¹³C{¹H} NMR (CD₂Cl₂): δ 21.1 (ArCH₃), 44.6 (CH₂), 126.8 (ArC), 129.7 (ArC), 135.5 (ArC), 144.6 (ArC). ¹¹B{¹H} NMR (CDCl₃): δ 21.4. IR (Nujol): 2148 cm⁻¹.

4d: crude product was used; yield 3.55 g (94%) of a slightly yellow solid. ¹H NMR (CDCl₃): δ 3.47 (s, 4 H, CH₂). ¹³C{¹H} NMR (CDCl₃): δ 37.3 ppm (CH₂). ¹¹B{¹H} NMR (CDCl₃): δ 65.6.

5: no purification necessary; yield 8.32 g (96%) of a colorless solid. ¹H NMR (CDCl₃): δ 1.34 (d, 6.2 Hz, 12 H, OCH(CH₃)₂), 4.66 (sep, 6.2 Hz, 2 H, OCH(CH₃)₂). ¹³C{¹H} NMR (CDCl₃): δ 24.7 (OCH(CH₃)₂), 69.8 (OCH(CH₃)₂). ¹¹B{¹H} NMR (CDCl₃): δ 20.5. IR (Nujol): 2151 cm⁻¹. **6**: product washed with benzene and pentane; yield 1.53 g (95%) of a faintly yellow solid. ¹H NMR (CDCl₃): δ 7.14 (s, 2 H). ¹³C{¹H} NMR (CDCl₃): δ 98.8 (CH), 143.8 (OC). ¹¹B{¹H} NMR (CDCl₃): δ 25.1. IR (KBr): 2149 cm⁻¹.

Gas-Phase Functionalization of Methane. Methane (4.5) was passed through two glass coils (d = 0.5 cm, l = 6 m) immersed in baths held at -78 and 30 °C, and two drying columns loaded with molecular sieves and silica gel in order to remove traces of water. Dry methane was bubbled through a neat sample of liquid PinBN₃ (4a; 3.00 g, 17.75 mmol) at room temperature and atmospheric pressure. The obtained gas mixture was passed through a quartz tube (d = 1.7 cm, l = 55 cm) and continuously photolyzed (36-48 h) using the output of a lowpressure mercury lamp (length of photolysis zone approximately 25 cm). Formation of a solid product was observed in the exposition zone and behind it during photolysis. After photolysis the apparatus was flushed with argon and the photoproduct was removed by dissolution in dry CH₂Cl₂ and washed into a Schlenk tube. After removal of the CH₂Cl₂ in vacuo and dissolution in 15 mL of dry Et₂O, the catalyst DMAP (N,N-dimethylaminopyridine) and acetyl chloride (AcCl; 0.60 mL, 8.436 mmol) were added. The resulting suspension was stirred for 18 h at room temperature. Then solid NaOH (0.50 g, 12.50 mmol) was added, and the reaction mixture was stirred for one more day. Afterward cycloheptylamine (internal standard; 0.501 g, 1.7752 mmol) in 15 mL of Et₂O was added, the mixture was filtered, and the solid was washed with Et₂O (3×8 mL). The filtrate was separated, and the mixture was analyzed by GC-MS and GC.

Single-Crystal X-ray Analysis. The X-ray intensity data for 4c and 11c were measured with graphite-monochromated Mo K α radiation on an Oxford Diffraction Xcalibur2 diffractometer with a Sapphire2 CCD. The CrysAlis^{Pro} software¹¹³ was used for the data collection and data reduction. A semiempirical absorption correction based on multiple-scanned reflections was applied.¹¹⁴ All crystal structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.¹¹⁵

Theory. The borylnitrenes were computed using the complete basis set CBS-QB3 extrapolation scheme of Petersson et al.^{91,92} as implemented in the Gaussian 09¹¹⁶ program. The CBS-QB3 scheme employs geometry optimizations and harmonic vibrational frequency computations using Becke's¹¹⁷ three-parameter hybrid functional in conjunction with the correlation functional of Lee, Yang, and Parr¹¹⁸ (B3LYP) along with higher level energy evaluations to extrapolate to the complete basis set energy. For comparison, the geometries of the three borylnitrenes given in Figure 5 were also computed using coupled cluster theory with single, double, and a perturbative estimate of triple excitations, CCSD(T),^{119,120} using analytic gradient techniques.¹²¹ All electrons were considered in the correlation treatment. The basis set employed was Dunning's¹²² triple- ζ basis set (10s6p contracted to 5s3p) with two sets of polarization functions.¹²³ The CCSD(T) calculations were performed with the CFOUR program.¹²⁴

The hydrogen-bonded dimer of 13a was computed using secondorder Møller–Plesset (MP2) perturbation theory within the frozen core approximation. The spin component scaling technique, introduced by Grimme¹²⁵ and known to improve MP2 energies, was used. The resolution of the identity (RI) approximation was also employed,¹²⁶ as it reduces the time required for the MP2 treatment while introducing only negligible errors. The def2-TZVP basis set was employed, along with the recommended fitting basis set required for the RI approximation.¹²⁷ The SCS-MP2 computations were performed with the Turbomole program.^{128,129}

ASSOCIATED CONTENT

Supporting Information

Text giving the complete refs 113 and 121, tables giving Cartesian coordinates and electronic energies for all computed species, and CIF files giving X-ray crystallographic data for 4c, 11c, and tetrachlorocatechol trihydrate. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: holger.bettinger@uni-tuebingen.de.

Notes

The authors declare no competing financial interest.

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