Borylnitrenes: electrophilic reactive intermediates with high reactivity towards C–H bonds

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Borylnitrenes (catBN **3a** and pinBN **3b**; cat = catecholato, pin = pinacolato) are reactive intermediates that show high tendency towards insertion into the C–H bonds of unactivated hydrocarbons. The present article summarizes the matrix isolation investigations that were aimed at identifying, characterizing and investigating the chemical behaviour of **3a** by spectroscopic means, and of the experiments in solution and in the gas phase that were performed with **3b**. Comparison with the reactivity reported for difluorovinylidene **1a** in solid argon indicates that **3a** shows by and large similar reactivity, but only *after* photochemical excitation. The derivative **3b** inserts into the C–H bonds of hydrocarbon solvents in high yields and thus allows the formation of primary amines, secondary amines, or amides from "unreactive" hydrocarbons. It can also be used for generation of methylamine or methylamide from methane in the gas phase at room temperature. Remaining challenges in the chemistry of borylnitrenes are briefly summarized.

Introduction

The formal isoelectronic substitution of a CC by a BN unit has long been known to produce compounds that have properties similar to their organic counterparts.[1] Notable examples from the molecular sciences are borazine, the "inorganic" benzene,[2] the more recently described 1,2-dihydro-1,2-azaborine[3] that links benzene and borazine, or iminoboranes RBNR,[4] the "inorganic" alkynes RCCR. The reactivity of the BN compounds is generally higher than that of the carbon parents due to the polarity and the lower strength of the B–N bond.[4]

We are interested in exploring the properties of compounds that may be considered as BN analogues of typical organic reactive intermediates. For example, isoelectronic substitution of the CC unit in vinylidenes **1** and the two dehydro carbon atoms in 1,2-didehydrobenzenes **2** by BN gives the regioisomeric borylnitrenes **3** and aminoborylenes **4**, and 1,2-azaborine **5**, respectively (Chart 1). Borylnitrenes and aminoborylenes can be stabilized in the coordination sphere of transition metals,[5,6] but direct spectroscopic detection of a "free" borylnitrene was not achieved prior to our work.[7] Parent aminoborylene H_2NB, on the other hand, was identified among the products formed during

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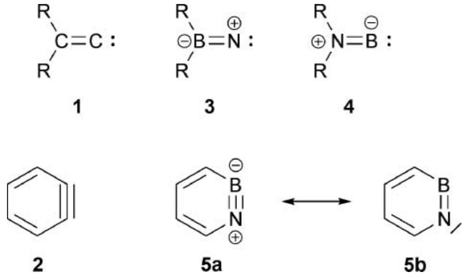


Chart 1 Vinylidene **1**, *ortho*-benzyne **2** and the corresponding BN analogues borylnitrenes **3**, aminoborylenes **4**, and 1,2-azaborine **5**.

co-deposition of boron atoms and ammonia.[8] The parent 1,2-azaborine was the subject of theoretical investigations,[9] but it is not known experimentally.

We here summarize our research in the field of borylnitrenes, compare their properties to those of vinylidenes, and note remaining challenges in their chemistry.

Theoretical considerations

Parent imidogen HN prefers the triplet state ($X^3\Sigma^-$) by 36.3 kcal mol^{-1} over the lowest energy singlet state ($a^1\Delta$).[10] Likewise, organic nitrenes RN prefer a triplet diradical ground state unless electronic effects of substituents change this.[11]

Aryl nitrenes have been the subject of considerable interest. The prototypical phenylnitrene has a triplet ground state ($\sigma^1\pi^1$, $^3A_2$) followed by "open-shell" ($\sigma^1\pi^1$, $^1A_2$) and "closed-shell" (π^2, $^1A_1$; σ^2, $^1A_1$) singlet states that are of multiconfiguration character.[12,13] The neighbouring carbonyl group[14] in acyl [RC(O)N] and oxycarbonyl [ROC(O)N] nitrenes strongly modifies the relative energies of electronic states due to bonding interactions between the oxygen and nitrogen atoms: acyl nitrenes thus seem to prefer singlet ground states.[15]

The boron centre in prototypical borylnitrene H_2BN can act as an electron acceptor and can stabilize the "closed-shell" singlet (π^2, $^1A_1$) with respect to the triplet state ($\sigma^1\pi^1$, $^3A_2$). Indeed, the π^2 singlet drops 7 kcal mol^{-1} below the triplet state in C_{2v} symmetric H_2BN.[7] The comparative analysis of the frontier molecular orbitals of H_2CC, H_2NB, and H_2BN using density functional theory shows that the LUMO energy is lowest for H_2BN (Fig. 1).[16] This should endow the borylnitrene with an electrophilicity that is larger than that of vinylidene H_2CC. Computational investigations by Nguyen[17] and by our group[7] reveal, however, that the C_{2v} structure of H_2BN does not correspond to a minimum on the potential energy hypersurface. Releasing the symmetry constraint results in linear iminoborane HBNH after complete geometry optimization. Hence, the parent borylnitrene does not correspond to an observable intermediate.

The instability of H_2BN deduced from theory is in agreement with experimental investigations. Thermolysis of dialkyl and diaryl azidoboranes (R_2BN_3) and N-trimethylsilyl-*N*-(trimethylsilyloxy)aminoboranes [$R_2BN(OSiMe_3)SiMe_3$] is concluded to yield iminoboranes without intermediate formation of borylnitrenes.[18] The latter could only be trapped in the photolysis of certain diamino substituted azidoboranes ($(R_2N)_2BN_3$).[19]

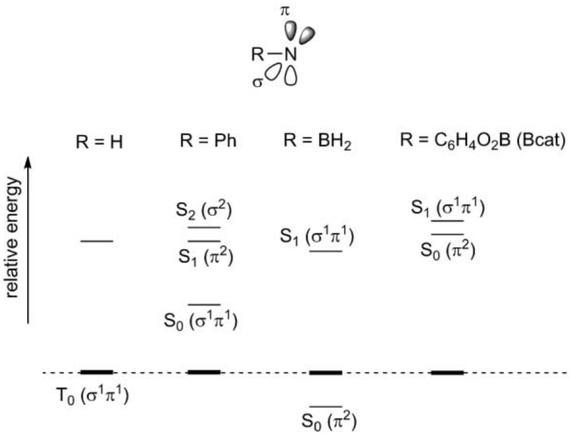
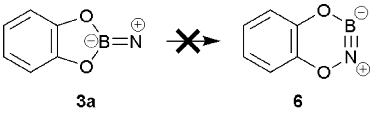


Fig. 1 Energies of nitrene RN singlet states relative to the lowest energy triplet state of $\sigma^1\pi^1$ configuration depending on the substituent R. Data for R = H, Ph are from experiment, while those for R = BH_2, cat were obtained at the CISD+Q/cc-pVTZ//(*n*,*m*)-CASSCF/6-31G* level of theory (*n* = *m* = 10 for R = BH_2; *n* = 12, *m* = 11 for R = cat).[7]

We reasoned that the strong boron–oxygen bonds as in 2-nitreno-1,3,2-benzodioxaborole **3a** (catBN; cat = catecholato) should suppress the rearrangement to a highly strained cyclic iminoborane **6** (Scheme 1). Indeed, a preliminary computational investigation showed that the putative cyclic iminoborane does not correspond to a stationary point at the B3LYP/6-311+G** level of theory as during attempted geometry optimization the nitrene **3a** was obtained.



Scheme 1 Singlet borylnitrene **3a** is computed to not undergo a rearrangement to the cyclic iminoborane **6**.

As expected, the introduction of B–O bonds reduces the Lewis acidity of the boron centre. Consequently, the π^2 singlet state is not the lowest energy state of nitrene **3a**. The triplet ($\sigma^1\pi^1$, $^3A_2$) state of C_{2v} symmetric **3a** is more stable than the most favorable singlet (π^2, $^1A_1$) by 33 kcal mol^{-1}. In contrast to the situation in phenylnitrene, the "open-shell" singlet state ($\sigma^1\pi^1$, $^1A_2$) is higher in energy than the π^2 state, but only by 1.4 kcal mol^{-1} according to configuration interaction (CI) computations that employ a two-configuration reference for the π^2 state.[7]

Matrix isolation studies

Isolation of the known[20] azide **7a** in cryogenic matrixes is straight forward and allows measuring its IR and UV spectra.[21] Upon photolysis with the output of a low pressure mercury lamp (λ = 254 nm) the azide quickly decomposes and the initially colourless matrix changes to orange–red. The IR, UV, and ESR spectra obtained after decomposition of the azide are in agreement with the formation of borylnitrene **3a**. Of particular importance is the typical triplet ESR spectrum with $|D/hc|$ = 1.492 cm^{-1} and $|E/hc|$ = 0.004 cm^{-1}, and the highly structured UV spectrum that extents up to almost 600 nm.

Irradiation into the lowest wavelength absorption with visible light (λ > 550 nm) produces the first surprise: the azide is formed back by reaction with nitrogen molecules that are formed in the initial photodecomposition and that lie close to **3a**. Changing the matrix host from argon to $(^{15}N)_2$ allows the photogeneration of **3a**-$[^{15}N]_2$ due to reaction of **3a** with the surrounding labelled nitrogen. Although it was mentioned by Hayes and Sheridan that phenylnitrene regenerates some phenylazide upon irradiation,[22] the reaction of nitrenes with N_2 is rather unusual. It should be noted that the formation of the azide **7a** from nitrene **3a** requires photochemical excitation: annealing of the matrix does not initiate any reaction of the nitrene. Indeed, even after complete evaporation of the matrix host at 55 K no azide is formed. IR and UV spectroscopy indicate formation of a new species, possibly the dimer catBNNBcat or an oligomer.[23,24] Attempts to isolate it at room temperature have been unsuccessful so far.

We subsequently studied the reactivity of **3a** by doping the matrix with possible trapping reagents including CO, H_2, CH_4, C_2H_4, C_2H_2, CF_4, and some isotopomers (see Scheme 2). Reactions could be observed with CO, H_2 (D_2), CH_4, and C_2H_4 after the photodecomposition of the azide (λ = 254 nm) and after visible light irradiation (λ > 550 nm) of the nitrene **3a**. Again, no thermally initiated reactions are observed between **3a** and trapping reagents. The products are the expected isocyanate **8**,[7] and the aminoboranes **9** and **10**,[25] in the reactions with CO, H_2, and CH_4, respectively. Unfortunately, we were not able to identify the product of the reaction with C_2H_4. The spectra obtained show some deviation from those computed for the aziridine **11** or the enamine **12** (Chart 2). Nitrene **3a** does not react with CF_4.[26] Attempts to react it with ethyne surprisingly failed.[27]

11 **12**

Chart 2 Aziridine **11** and enamine **12** could not be identified as products in the reaction of **3a** with ethylene.

We could also observe a thermal reaction of **3a**: annealing of **3a** in an argon matrix to 35 K in the presence of molecular oxygen produces the nitroso-*O*-oxide **13** that is unstable photochemically and rearranges to the nitritoborane **14** upon short wavelength irradiation.

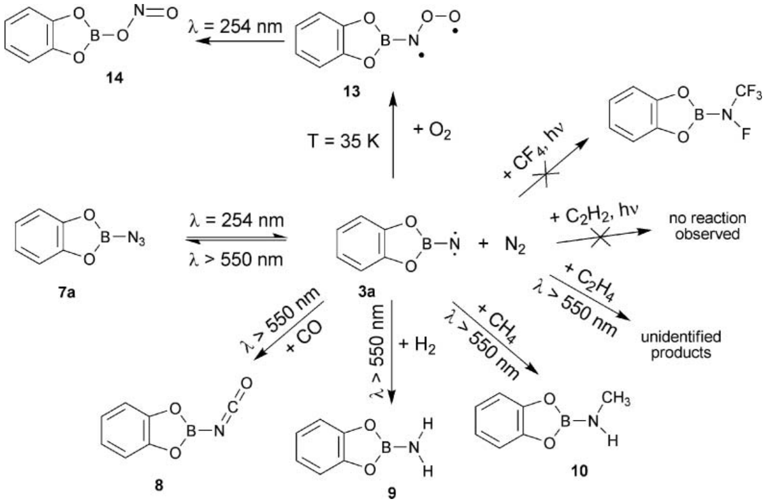
Comparison of the chemistry observed for **3a** with that of difluorovinylidene **1a** (R = F) is instructive. Sander and co-workers could generate **1a** photochemically from difluoroacetylene in matrixes and could observe a number of interesting reactions, including the complexation with Xe, addition to CC multiple bonds and insertion into C–H bonds, upon *thermal* activation of **1a**.[28] This led them to call **1a** a "super-electrophilic" carbene.[29] Nitrene **3a** shows similar reactivity (see Scheme 2), but it requires photochemical activation, presumably to generate the vinylidene-like highly electrophilic singlet state. In particular, **3a** readily inserts into the C–H bonds of methane and into dihydrogen (or dideuterium), and just as **1a**, it does not insert into C–F bonds. In contrast to **1a** that readily adds to CC multiple bonds, we could not identify the products of reaction with ethene and could not observe a reaction with ethyne. Likewise, formation of a Xe compound was not observed.

Solution phase C–H insertion

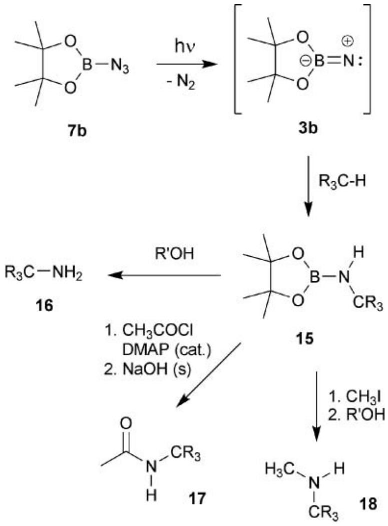
The insertion of nitrenes RN into C–H bonds is well established. Intermolecular C–H insertions are mostly limited to highly electrophilic nitrenes such as fluorinated phenyl (R = $C_6H_nF_{5-n}$),[30] cyano (R = NC),[31] acyl (R = R′CO),[32] and oxycarbonylnitrenes (R = R′OCON)[33] as well as the "inorganic" sulfonyl [R = $R'S(O)_2$][34] and phosphorylnitrenes [R = $(R'O)_2P(O)$].[35] The yield of insertion products varies strongly and is close to quantitative for phosphorylnitrenes.[35]

The high reactivity of **3a** that we observed under matrix isolation conditions, in particular the tendency to insert into strong covalent bonds, prompted us to also investigate its properties in solution.

We found that the photolysis of azide **7a** in cyclohexane produced polymeric material that could not be characterized satisfactorily. This could be due to the known tendency of catBNHR aminoboranes to oligomerize.[36] We thus investigated the nitrene **3b** accessible from azido pinacolborane **7b**. We indeed obtained a high yield of insertion product after photolysis in hydrocarbon solvents (see Scheme 3).[25a] The corresponding aminoboranes **15** could



Scheme 2 Reactivity observed for triplet nitrene **3a** under matrix isolation conditions.



Scheme 3 Photogeneration of borylnitrene **3b**, its C–H insertion and possible ways of functionalization of the resulting aminoboranes **15**.

be structurally characterized for cyclopentane,[25a] cyclohexane,[25a] and cycloheptane[37] C–H insertion. The yields after isolation by sublimation reach 85% and are thus similar to those reported by Breslow *et al.*[35a] for $(EtO)_2P(O)N$.

The aminoboranes of type **15** can be functionalized further: hydrolysis or alcoholysis yields the free primary amines **16**, while acylation in the presence of *N*,*N*-dimethylaminopyridine (DMAP) yields amides **17** after cleavage of the B–N bond by hydroxide or fluoride anions.[25a] It is also possible to methylate **15** and obtain the secondary amine **18** after alcoholysis.[37]

The reaction in 2,3-dimethylbutane reveals that the insertion is statistical within the limits of GC detection,[25a] similar to that observed for diethoxyphosphorylnitrene.[35a] The competition experiment using cyclohexane and perdeuterocyclohexane reveals a small kinetic isotope effect of 1.35.[37] Following Maslak's analysis of diethoxyphosphorylnitrene,[35b] the small kinetic isotope effect may be associated with a small barrier for C–H insertion of nitrene **3b**. The computed barrier of insertion into the H–H bond for a model system of **3a** is about 1 kcal mol^{-1} at the CASSCF/6-31G* level and vanishes upon inclusion of dynamical correlation at the MRPT2 level of theory.[25b]

Gas phase C–H insertion

The high reactivity of **3b** also allows gas phase intermolecular insertion reactions. It is indeed possible to transform methane at room temperature and ambient pressure into methylamine or N-methylamides.[37] When this is done in a flow system that allows photolysis of a mixture of azide **7b** and methane, it is possible to obtain a yield of 6–8% based on **7b** after workup. Control experiments in argon atmosphere show that the methylamine or N-methylamides obtained are not resulting from an intramolecular rearrangement of a methyl group from the pinacol backbone. Under the gas phase conditions it is also possible to obtain ammonia and hydrazine derivatives after acylation, and their yield strongly increases in an argon atmosphere. These products might be due to hydrogen abstraction and dimerization of triplet nitrene **3b** or of aminyl radicals that form from triplet **3b** by hydrogen abstraction. Clearly, the low pressure in the photolysis flow system results in much longer free paths between reactive collisions and allows relaxation of the highly electrophilic singlet **3b**-S to the less reactive triplet **3b**-T. Another reason for the low yield may be the low absorbance of **7b** at 254 nm that in combination with the short time of **7b** in the photolysis zone results in a low yield in the photochemical transformation. However, in principle the residence time and the pressure can be increased and the unreacted azide can be recycled.

Opportunities and remaining challenges

The investigation of the chemical properties of this class of reactive intermediates is of fundamental interest. In this context, the reactions of **3a** (under matrix isolation) or **3b** (in solution phase) with unsaturated hydrocarbons remain to be clarified. In solutions, the strong absorbance of unsaturated hydrocarbons like 2,3-dimethyl-2-butene and aromatics at the wavelength used for photodecomposition of **7b** complicate the analysis of reaction products. Azidoboranes that absorb at significantly longer wavelengths than **7a** or **7b** are thus highly desirable.

It is obvious that a species that cannot discriminate between primary and tertiary C–H bonds in insertion reactions as observed for **3b** is of limited use in organic synthesis. Indeed, the reactivity observed so far for **3b** is reminiscent of that of singlet methylene, the "*most indiscriminate reagent known in organic chemistry*".[38]

One approach to more selective (and presumably less reactive) borylnitrenes may be the modification of the ligands by judiciously employing electronic or steric effects. It would be particularly desirable to modify the electronic structure so that a singlet ground state results for the borylnitrene. Alternatively, transition metal mediated decomposition of the borylazides might provide access to more selective $L_nM\text{-}NBR_2$ species. Early transition metal atoms in high oxidation states form stable complexes, *e.g.*, by decomposition of Mes_2BN_3.[5a] Recent success in the utilization of azides as nitrene sources in transition metal mediated transformations has been reported,[39] but it remains to be seen if these systems are compatible with borylazides.

Conclusions

Oxygen ligated borylnitrenes emerge as a new class of highly electrophilic nitrenes. Under matrix isolation conditions, the catechol derivative **3a** is a triplet species that reacts thermally already at 35 K with molecular oxygen. Upon photoexcitation **3a** shows high reactivity: it adds to N_2 and CO, inserts into a C–H bond of methane and into the H–H (D–D) bond of dihydrogen. Theory indicates that the high reactivity is due to the high electrophilicity that arises from the empty in-plane p orbital centred at the N atom in the singlet state.

The high reactivity of borylnitrenes is not limited to matrix isolation conditions. Photodecomposition of the pinacol derivative **7b** yields transient nitrene **3b** that inserts into C–H bonds of alkanes in high yield. Its insertion reactions are, however, indiscriminate with respect to the strength of the C–H bonds. The high reactivity towards C–H insertion even allows the transformation of methane at room temperature and ambient pressure. The primary insertion products, aminoboranes, can be reacted further to primary or secondary amines or to amides.

Acknowledgements

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