

Insertion into dihydrogen employing the nitrogen centre of a borylnitrene†

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A borylnitrene, accessible from the corresponding azide by UV photolysis in a solid D₂ matrix at 3 K, inserts into D₂ upon visible light irradiation under cryogenic conditions.

The activation of dihydrogen, a traditional stronghold of transition metal chemistry,¹ has seen considerable advances lately through the utilization of main group element compounds. Recent achievements in splitting of the H–H bond have been made using stable carbenes,² “frustrated Lewis pairs” and related systems,³ and a digermene compound,⁴ but also strong base under harsh reaction conditions is known to effect hydrogenation.⁵ Bertrand and co-workers demonstrated the splitting of dihydrogen by the subvalent carbon center of a *stable* carbene at room temperature and pointed out the isolobal analogy between carbenes and coordinatively unsaturated transition metals.² While this analogy may prove helpful in the development of novel catalytic systems, the insertion into the H–H bond is well-known for *transient* carbenes. For example, super-electrophilic carbenes,⁶ like singlet difluorovinylidene and triplet fluorinated and chlorinated 4-oxo-cyclohexa-2,5-dienylidenes, have been shown by Sander and his group to insert into dihydrogen already at 35 K without photochemical activation.^{7,8} A number of other main group systems, including the subvalent CH₂, also insert into the H–H bond in gas phase reactions, under matrix isolation conditions, or under ambient conditions.^{9–11}

Nitrenes, the subvalent nitrogen analogues of carbenes, should also be able to split dihydrogen based on their electron deficiency and the strength of the resulting N–H bonds. We have recently discovered that the borylnitrene **1**, related to vinylidenes by the substitution of the CC unit by its iso-electronic BN counterpart,¹² is highly reactive even at cryogenic temperatures.¹³ For example, **1** reacts readily upon visible light irradiation ($\lambda > 550$ nm) with N₂ and it inserts into the C–H bond of methane under cryogenic conditions as well as into the C–H bonds of (cyclo)alkanes at room temperature in solution in good yields.¹³ In view of the similar strengths of the C–H bond in methane and the H–H bond [BDE(H₃C–H) = 104.8 kcal mol^{−1},

BDE(H–H) = 104.2 kcal mol^{−1}],¹⁴ splitting of dihydrogen by **1** can indeed be achieved at cryogenic temperatures upon photochemical excitation as reported here.

Borylnitrene **1** is accessible from the corresponding azide **2** by UV photolysis. Hence, when **2** was isolated in a deuterium matrix at 3 K and irradiated ($\lambda = 254$ nm), signals due to nitrene **1** in its triplet state grew while those arising from **2** concomitantly decreased in intensity. In addition, another set of signals was observed to form during UV photolysis of **2**; among them are prominent absorptions at 2667 and 2542 cm^{−1} that are assigned to the asymmetric and symmetric N–D stretching vibration indicating the formation of N–D bonds. In a hydrogen doped neon matrix these signals are observed at 3571 and 3482 cm^{−1}. The measured H/D isotopic shifts, 1.339 and 1.369, for the asymmetric and symmetric stretching vibration, are in good agreement with the ones calculated (1.353 and 1.382) for the aminoborane **3** and supports the assignment of the corresponding set of signals to the D₂ (or H₂) insertion product **3** (see ESI†). As **3** is unknown and certain catecholborylamines form oligomers or polymers easily,¹⁵ no attempts have been made to synthesize an authentic sample of **3**.

We have observed earlier that irradiation into the long wavelength tail of the electronic absorption of **1** can initiate its reactions with “inert” closed-shell molecules like N₂, CO, and CH₄.¹³ This is also observed for the reaction with D₂: upon visible light excitation ($\lambda > 550$ nm), signals assigned to **3** increase further in intensity, while those of **1** disappear quickly (Fig. 1). The reaction of **1** with molecular nitrogen lying in its vicinity back to the azide **2** during long wavelength photolysis, which we observed earlier, is suppressed in the

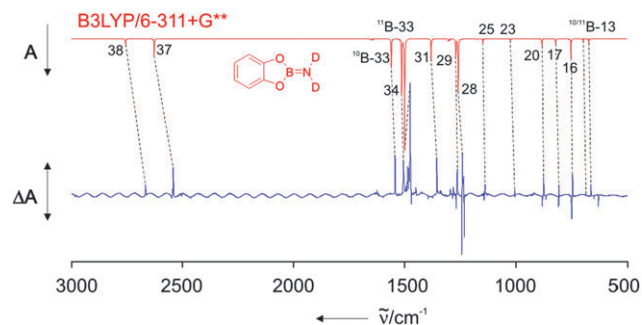
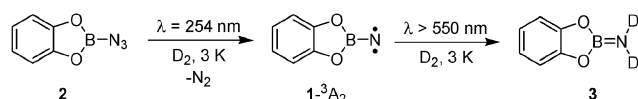


Fig. 1 Bottom: difference spectrum obtained after long wavelength photolysis ($\lambda > 550$ nm) of a deuterium matrix including borylnitrene **1** which was generated in a first step from azide **2** by UV irradiation ($\lambda = 254$ nm; not displayed). Signals pointing downwards are due to **1** and decrease, those pointing upwards are assigned to **3** and increase during irradiation with $\lambda > 550$ nm light. Top: IR spectrum computed for **3** of C_{2v} symmetry at the B3LYP/6-311 + G** level of theory.

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Scheme 1 Photoreactions of **2** and **1** in solid deuterium at 3 K.

deuterium matrix. But this competing pathway is observed if the concentration of trapping agent is reduced by using neon matrices containing only a few percent of D₂ or H₂.

The investigation of the photoreaction in solid D₂ by ESR spectroscopy confirms that the free nitrene is formed in its triplet ground state during UV irradiation. The zero field splitting (ZFS) parameters, $|D/hc| = 1.508 \text{ cm}^{-1}$ and $|E/hc| = 0.003 \text{ cm}^{-1}$, are similar but not identical to the values obtained in an argon matrix ($|D/hc| = 1.492 \text{ cm}^{-1}$ and $|E/hc| = 0.004 \text{ cm}^{-1}$)^{13a} indicative of somewhat different environments in these matrix host gases. Subsequent long wavelength irradiation ($\lambda > 550 \text{ nm}$) results in a decrease in the ESR transition of **1** indicative of a photoreaction. From the combination of our experimental data the reactions displayed in Scheme 1 can be deduced.

A computational investigation of the reaction between borylnitrene **1** and H₂ provides further insight. We have chosen complete active space self consistent field (CASSCF) theory distributing 12 electrons over 12 active orbitals (see ESI for selection†) for determining geometries in conjunction with the 6-31G* basis set as our earlier computations revealed pronounced multiconfiguration character for the ¹A₁ state of **1**.^{13a,16} Energies are refined by multireference second-order perturbation theory (MRPT2) single point computations. The geometry of the TS (350i cm⁻¹) for the addition of H₂ to **1** is indicative of a dative interaction between the vacant in-plane p orbital at the nitrene center N(p) and the σ orbital of the H–H bond as the H₂ molecular axis is oriented almost perpendicularly to the molecular plane of **1**. But it is of non-least motion nature, as its structure slightly deviates from C_s symmetry as evidenced by differing N···H distances of 2.009 and 2.047 Å. The computation of the intrinsic reaction coordinate confirms that the TS indeed connects C_{2v} symmetric aminoborane **3** with **1** + H₂ (Fig. 2).

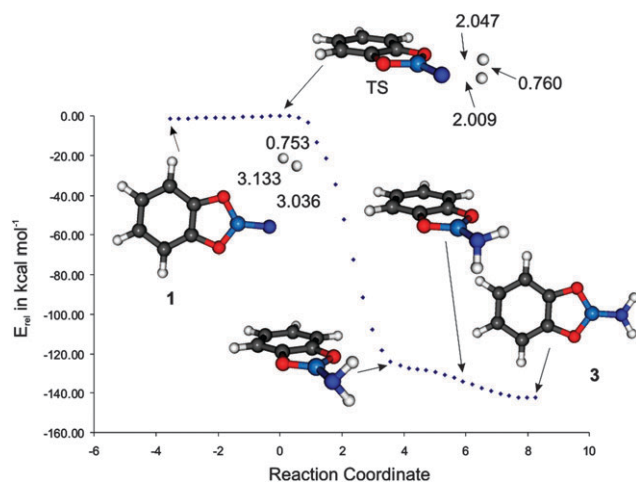


Fig. 2 The intrinsic reaction coordinate (IRC) computed for the addition of H₂ to borylnitrene **1** at the (12,12)-CASSCF/6-31G* level of theory. Distances between H and between H and N atoms are given in Å.

The computations further confirm the expected strongly exothermic nature of the formation of **3** from ¹A₁-**1** + H₂, $\Delta_R H^\circ(0 \text{ K}) = -145 \text{ kcal mol}^{-1}$. The barrier for the reaction is very small, 1.3 kcal mol⁻¹, at the CASSCF level of theory. Inclusion of electron correlation effects at the MRPT2 level lowers the energy of the TS below that of the reactant complex, indicating that at this level a barrier is not existing on the classical potential energy surface.

In summary, our investigation of the photochemistry of borylazide **2** in solid deuterium and neon matrices doped with hydrogen or deuterium reveal that the borylnitrene **1** is reactive enough to insert into the H–H bond after photochemical excitation of its triplet ground state. We ascribe the high reactivity of **1** to the closed-shell nature of its lowest lying singlet state that is vinylidene-like.^{13a} The computational investigation of the reaction from the lowest energy singlet state of **1** reveals that the insertion can possibly proceed without any barrier on the potential energy surface.¹⁷ The splitting of dihydrogen by **1** is further testimony to the unusually high reactivity of **1** observed earlier in the reactions with N₂ and CH₄.¹³

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