Supporting Information

Insertion into dihydrogen employing the nitrogen centre of a borylnitrene

Holger F. Bettinger,[a,b,]* Matthias Filthaus,[a] and Patrik Neuhaus[a]

[a] *Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, Universitätsstrasse 150, 44780 Bochum, Germany*

[b] *Instiut für Organische Chemie, Eberhard Karls Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany*

holger.bettinger@uni-tuebingen.de

I. Experimental and Computational Details

The azide **2** was synthesized as described previously.[1]

Matrix experiments. Matrix experiments were carried out using standard techniques[2] with and Sumitomo closed-cycle helium cryostats. Matrices were produced by codeposition of a large excess of deuterium or mixtures of deuterium with neon (Messer-Griesheim, 99.9999%) and hydrogen (UCAR, ultra high purity) with neon and the azide **2** held at 0 °C by means of an ice bath on top of a cold CsI or quartz window. During the deposition the temperature of the window was maintained at 3 K. IR spectra were recorded with Bruker IFS 66/S FTIR spectrometer with a resolution of 0.5 cm^{-1} in the range of 400 − 4000 cm^{-1}. EPR spectra were recorded with a Bruker Elexsys E500 spectrometer. The computer simulation of the EPR spectrum of **3** was performed by using the XSophe computer simulation software suite (version 1.0.4),[3] developed by the Centre for Magnetic Resonance and Department of Mathematics, University of Queensland, Brisbane (Australia) and Bruker Analytik GmbH, Rheinstetten (Germany). The simulation was performed by using a matrix diagonalization method for S = 1 and setting the parameters ν_0 = 9.60934 GHz, g = 2.0023, |D/hc| = 1.508 cm^{-1} and |E/hc| = 0.003 cm^{-1}. Irradiations were carried out with a Gräntzel low pressure mercury lamp (254 nm) and an Osram HBO-500-W/2 high pressure mercury lamp in an Oriel housing with quartz optics, a dichroic mirror (420 − 680 nm), and a Schott cutoff filter (550 nm).

Computations. Geometry of **3** was optimized and vibrational frequencies were obtained using the B3LYP[4] functional in conjunction with the 6-311+G** basis set as included in the Gaussian 03 program.[5]

The CASSCF computation of the transition state for H–H insertion considered the lowest energy singlet state of boryl nitrene **1**, i.e., $^1A_1$. The active space was modified based on the 12 by 11 space (all 12 π electrons distributed over 10 π and one empty N(σ) orbital) employed in our previous investigation.[6] Correlation of the two π lone pairs of oxygen atoms is not essential as indicated by their high occupations numbers of 1.99. In view of the reduced symmetry from C_{2v} for **1** to C_1 for the TS of H_2 addition, these two π lone pairs of oxygen atoms were not included into the active space thus reducing it to 8 π electrons and 8 π orbitals. In addition, the σ/σ* orbitals and the electron pair of the H–H molecule as well as the N(sp) lone pair and the vacant N(p) were included resulting in a 12 by 12 active space, (12,12)-CASSCF. In view of the large active space the 6-31G* basis set was used for the CASSCF calculations. Harmonic vibrational frequencies were computed analytically and the intrinsic reaction coordinate was computed using the default values of the GAMESS program.[7] Energies were refined by single state multiconfiguration perturbation theory (MRMP2) single point computations with identical active spaces again using the 6-31G* basis set. The CASSCF and MRMP2 calculations were performed with GAMESS.[7]

As we have observed earlier[6] that the multiconfiguration nature of borylnitrene **1** is handled well by coupled cluster theory with singles, double, and a perturbative estimate of triple excitations [CCSD(T)][8] in conjunction with the correlation consistent triple-ζ basis set,[9] this method has also been used for single point computations employing the (12,12)-CASSCF/6-31G* geometries. The MOLPRO[10] program was employed for all CCSD(T) runs.

II. Cartesian Coordinates and Energies of 2-amino-1,3,2-benzodioxaborole (**3**) as computed at the B3LYP/6-311+G** level of theory.

```
Method:     B3LYP/6-311+G**
Stoichiometry    C6H6BNO2
 Framework group  C2V[C2(BN),SGV(C6H6O2)]
 Deg. of freedom    15
 Full point group                C2V     NOp   4
 Largest Abelian subgroup        C2V     NOp   4
 Largest concise Abelian subgroup C2     NOp   2
                         Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic     Atomic              Coordinates (Angstroms)
 Number     Number      Type              X           Y           Z
 ---------------------------------------------------------------------
    1          6           0        0.000000    0.697718   -2.545609
    2          6           0        0.000000    1.427217   -1.347544
    3          6           0        0.000000    0.697627   -0.175843
    4          6           0        0.000000   -0.697627   -0.175843
    5          6           0        0.000000   -1.427217   -1.347544
    6          6           0        0.000000   -0.697718   -2.545609
    7          8           0        0.000000    1.155020    1.124797
    8          5           0        0.000000    0.000000    1.916740
    9          7           0        0.000000    0.000000    3.313208
   10          8           0        0.000000   -1.155020    1.124797
   11          1           0        0.000000    2.509889   -1.335837
   12          1           0        0.000000   -2.509889   -1.335837
   13          1           0        0.000000   -1.231399   -3.488667
   14          1           0        0.000000    1.231399   -3.488667
   15          1           0        0.000000    0.849312    3.852027
   16          1           0        0.000000   -0.849312    3.852027
 ---------------------------------------------------------------------
 Rotational constants (GHZ):      3.8247061      1.0263398      0.8091962
SCF Done:  E(RB+HF-LYP) =  -462.571724363     A.U. after    1 cycles
             Convg  =    0.4284D-08             -V/T =  2.0039
             S**2   =   0.0000

        Item               Value     Threshold  Converged?
 Maximum Force            0.000014     0.000015     YES
 RMS     Force            0.000003     0.000010     YES
 Maximum Displacement     0.000029     0.000060     YES
 RMS     Displacement     0.000011     0.000040     YES
 Predicted change in Energy=-1.575223D-09
```

III. Cartesian Coordinates computed at the (12,12)-CASSCF/6-31G* level of theory.

1) Transition state for insertion of 1 into the H–H bond

```
THE POINT GROUP OF THE MOLECULE IS C1
 THE ORDER OF THE PRINCIPAL AXIS IS     0

 ATOM      ATOMIC                      COORDINATES (BOHR)
           CHARGE         X                   Y                   Z
 C           6.0    -4.8929550233       -1.1307364583       -0.0153855207
 C           6.0    -2.7233727731       -2.6677917247       -0.0296916160
 C           6.0    -0.4309610279       -1.4352116152        0.0003193867
 C           6.0    -0.2510300779        1.1864992218        0.0431946238
 C           6.0    -2.3520453653        2.7226728029        0.0586233381
 C           6.0    -4.7121702055        1.4984481856        0.0276305573
 O           8.0     1.9541490653       -2.4498521020       -0.0023247417
 B           5.0     3.5372681295       -0.3862505967        0.0360302177
 N           7.0     6.2309768265       -0.7881320580       -0.0471601739
 O           8.0     2.2523903031        1.8668079571        0.0670194270
 H           1.0    -2.8387199976       -4.6924678589       -0.0620931566
 H           1.0    -2.1886406443        4.7441073370        0.0921438686
 H           1.0    -6.4072397781        2.6164086984        0.0374732221
 H           1.0    -6.7253317364       -2.0054738739       -0.0380410562
 H           1.0     7.2168962849        2.8709668340        0.7263194970
 H           1.0     7.3477052021        2.7806281260       -0.7009335466

FINAL MCSCF ENERGY IS     -459.6247046191 AFTER   2 ITERATIONS
TOTAL MRPT2, E(MP2) 0TH + 1ST + 2ND ORDER ENERGY =      -460.8352363370

        CCSD(T)         HF-SCF
   -461.43954121   -459.65861510
```

2) Endpoint of the IRC calculation – forward side

```
THE POINT GROUP OF THE MOLECULE IS C1
 THE ORDER OF THE PRINCIPAL AXIS IS     0

 ATOM      ATOMIC                      COORDINATES (BOHR)
           CHARGE         X                   Y                   Z
 C           6.0    -4.9225573744       -1.0855819808       -0.0156888326
 C           6.0    -2.7834719123       -2.6641598871       -0.0329370203
 C           6.0    -0.4682325330       -1.4753169244       -0.0012442806
 C           6.0    -0.2366779327        1.1422515574        0.0463545344
 C           6.0    -2.3077863401        2.7187461471        0.0643985866
 C           6.0    -4.6905320173        1.5397468908        0.0316494260
 O           8.0     1.8990989139       -2.5400958324       -0.0078026797
 B           5.0     3.5092133297       -0.5085899292        0.0328106001
 N           7.0     6.2203794328       -0.7704804210       -0.0423279493
 O           8.0     2.2817454005        1.7742719517        0.0710904657
 H           1.0    -2.9372649042       -4.6861579931       -0.0691215151
 H           1.0    -2.1052587064        4.7364517942        0.1012122478
 H           1.0    -6.3636457777        2.6901593611        0.0434691719
 H           1.0    -6.7714769731       -1.9245135915       -0.0396943550
 H           1.0     7.3876127914        5.0295320281        0.1686690024
 H           1.0     8.6123918346        4.4394268912       -0.2527576779

FINAL MCSCF ENERGY IS     -459.6267380176 AFTER   2 ITERATIONS
TOTAL MRPT2, E(MP2) 0TH + 1ST + 2ND ORDER ENERGY =      -460.8341691132

        CCSD(T)         HF-SCF
   -461.43190571   -459.65801733
```

3) Endpoint of the IRC calculation – reverse side

```
THE POINT GROUP OF THE MOLECULE IS C1
 THE ORDER OF THE PRINCIPAL AXIS IS     0
```

```
 ATOM      ATOMIC                       COORDINATES (BOHR)
           CHARGE         X                   Y                   Z
 C           6.0    -4.8794527745       -1.1627351236       -0.0254289318
 C           6.0    -2.6869235383       -2.6687271462       -0.0769639839
 C           6.0    -0.4077410146       -1.4124046058       -0.0309434767
 C           6.0    -0.2606656397        1.2145565140        0.0621782602
 C           6.0    -2.3852557904        2.7173811192        0.1135907415
 C           6.0    -4.7322586173        1.4655106908        0.0674447440
 O           8.0     1.9797053755       -2.3910251649       -0.0652160463
 B           5.0     3.5740664738       -0.3173723663        0.0075865762
 N           7.0     6.2074404911       -0.4638126631        0.0002318159
 O           8.0     2.2210129135        1.9208857419        0.0879424761
 H           1.0    -2.7783987774       -4.6942158318       -0.1489010384
 H           1.0    -2.2498509460        4.7404385926        0.1849594217
 H           1.0    -6.4413938324        2.5621733522        0.1047190454
 H           1.0    -6.7003850746       -2.0618503197       -0.0586696746
 H           1.0     7.3245306097        1.0894214877        0.0508493930
 H           1.0     7.1458540123       -2.1308245451       -0.0596000902

FINAL MCSCF ENERGY IS     -459.8517262531 AFTER   2 ITERATIONS
TOTAL MRPT2, E(MP2) 0TH + 1ST + 2ND ORDER ENERGY =      -461.0631834796

        CCSD(T)         HF-SCF
   -461.67054182   -459.87344782
```

IV. Experimental and Computed Vibrational Data for **3**, CatBND$_2$.

Table S1. Computed and Experimental Vibrational Data of **3**.

	B3LYP/6-311+G**						**3** at 3 K in D$_2$ [a]			
		^{11}B Isotopomer		**^{10}B Isotopomer**		**^{11}B/^{10}B**	**^{11}B**	**^{10}B**	**^{11}B/^{10}B**	**rel. Int.**
number [b]	sym	ω/cm^{-1}	rel. Int.	ω/cm^{-1}	rel. Int.		$\tilde{\nu}$ /cm^{-1}	$\tilde{\nu}$ /cm^{-1}		
42	A_1	3204	0	3204	0	1.000				
41	B_2	3200	1	3200	1	1.000				
40	A_1	3187	2	3187	2	1.000				
39	B_2	3173	0	3173	0	1.000				
38	B_2	2757	5	2757	4	1.000	2666.6			w
37	A_1	2627	13	2627	12	1.000	2543.8 2541.5			m
36	A_1	1655	1	1657	4	0.999				
35	B_2	1646	1	1647	1	1.000	1625.3 [e]			vw
34	A_1	1516	49	1504	39	1.008	1506.5			s
33	A_1	1502	100[c]	1563	100[d]	0.961	1481.9 1493.8 1487.2	1544.3	0.960	vs
32	B_2	1496	0	1496	0	1.000				
31	A_1	1382	16	1383	12	1.000	1356.9			s
30	B_2	1302	1	1305	9	0.998	1296.4			
29	B_2	1272	16	1298	8	0.980	1264.4	1282.2 [e]	0.986	m
28	A_1	1261	40	1261	34	1.000	1236.4 1241.5			s
27	A_1	1176	1	1177	1	0.999				
26	A_1	1167	0	1171	0	0.996				
25	B_2	1149	4	1156	2	0.994	1139.5			w
24	B_2	1099	0	1103	0	0.996				
23	A_1	1026	2	1026	2	1.000	1006.0			w
22	A_2	973	0	973	0	1.000				
21	B_1	934	1	934	1	1.000	918 [e]			vw
20	A_1	884	6	884	5	1.000	875.0			m
19	B_2	881	1	882	1	1.000				

18	A_2	861	0	861	0	1.000				
17	A_1	822	3	822	3	1.000	806.9			w
16	B_1	752	15	752	14	1.000	744.9			m
15	A_2	745	0	745	0	1.000				
14	B_2	736	0	736	0	1.000				
13	B_1	673	4	697	3	0.965	661.9	686.3	0.964	w
12	A_1	635	0	636	0	0.999				
11	B_2	620	0	621	0	0.999				
10	A_2	581	0	581	0	1.000				
9	A_1	480	0	482	0	0.995				
8	B_2	445	0	447	0	0.995				
7	B_1	431	1	431	1	0.999	425.0 [d]			vw
6	A_2	339	0	339	0	1.000				
5	B_1	316	2	317	2	0.997				
4	B_1	274	14	274	13	0.999				
3	A_2	230	0	230	0	1.000				
2	B_2	225	0	225	0	0.998				
1	B_1	111	1	111	1	1.000				

[a] These signals increase during λ ≥ 550 nm irradiation. [b] Mode numbers taken from the computed spectrum. [c] Absolute intensity: 663.3 km mol^{-1}. [d] Absolute intensity: 755.7 km mol^{-1}. [e] Tentative assignment.

Table S2. Comparison of the bands disappearing during $\lambda \geq 550$ nm irradiation in solid D_2 at 3 K with those assigned previously to **1** isolated in solid argon at 10K.

D_2, $\tilde{\nu}$ /cm^{-1}	Ar, $\tilde{\nu}$ /cm^{-1} [b]	rel. Int. [b]
	3080	4
	3074	1
	3068	3
	3056	1
	1597	2
1598	1594	7
	1476	5
1471	1470	44
	1283	2
1270, 1287	1267, 1285	18
1245, 1234	1230, 1241	100
	1148	3
1144	1143	15
	1129	6
	1007	8
	924	4
881	880	11
865	865	10
809	809	36
749	745	66
649		
629	628	19
468	467	9

[a] Bands disappear during $\lambda \geq 550$ nm irradiation.
[b] Taken from Reference 6.

V. ESR Spectrum of 1 in solid deuterium at 4 K.

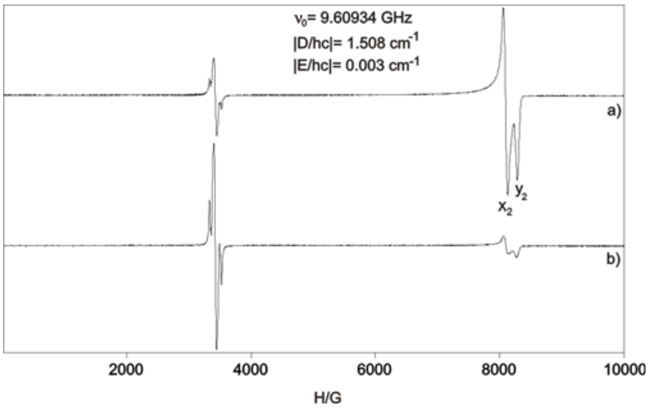

Figure. ESR spectra obtained during the irradiation of azide **2** isolated in a deuterium matrix at 4 K. Trace a) after 254-nm irradiation; trace b) after subsequent >550-nm irradiation.

References

[1] Fraenk, W.; Habereder, T.; Klapötke, T. M.; Nöth, H.; Polborn, K. *J. Chem. Soc., Dalton Trans.* **1999**, 4283.

[2] I. R. Dunkin, *Matrix Isolation Techniques: A Practical Approach*, Oxford University Press, Oxford, **1998**.

[3] Griffin, M.; Muys, A.; Noble, C.; Wang, D.; Eldershaw, C.; Gates, K. E.; Burrage, K.; Hanson, G. R. *Mol. Phys. Rep.* **1999**, *26*, 6084

[4] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 ;b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision B.4, Gaussian, Inc., Pittsburgh PA, **2003.**

[6] H. F. Bettinger, H. Bornemann, *J. Am. Chem. Soc.* **2006**, *128*, 11128.

[7] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347.

[8] a) K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479; b) C. Hampel, K. Peterson, H.-J. Werner, *Chem. Phys. Lett.* **1992**, *190*, 1; c) J. D. Watts, J. Gauss, R. J. Bartlett, *J. Chem. Phys.* **1993**, *98*, 8718; d) P. J. Knowles, C. Hampel, H.-J. Werner, *J. Chem. Phys.* **1993**, *99*, 5129.

[9] T. H. Dunning, *J.Chem.Phys.* **1989**, 90, 1007.

[10] MOLPRO, a package of *ab initio* programs designed by H.-J. Werner and P. J. Knowles, version 2002.1, R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, P. J. Knowles, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, and H.-J. Werner.