4206 *Inorg. Chem.* **2000,** *39,* 4206−4210

Ab Initio Study of Rearrangements on the $(CH)_2(BR)_2$, R=H, and NH_2 Potential Energy Surfaces[†]

Michael L. McKee*

Department of Chemistry, Auburn University, Auburn, Alabama 36849

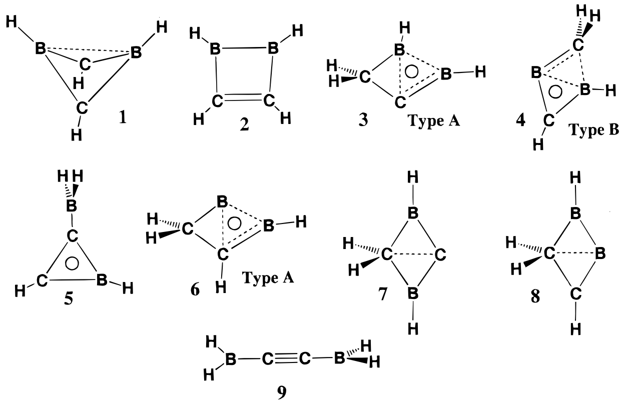
Received March 3, 2000

A comprehensive survey of the $(CH)_2(BH)_2$ potential energy surface was carried out at the [MP4/6-311+G(d,p)]//MP2/6-31G(d) level. Many of the classical and nonclassical isomers of the carborane surface are separated by high activation barriers, which explains why derivatives of most isomers could be prepared as stable compounds at room temperature. The transition states are grouped into two types, hydrogen migration (terminal-to-bridge and bridge-to-terminal) and group migration (BH, CH, and CH_2). The rearrangement of 1,3-diamino-1,3-diboretene (**1-NH$_2$**) to 1,2-diamino-1,2-diboretene (**2-NH$_2$**) was computed and compared to the rearrangement in the parent (**1** → **2**). The effect of the amino group is to substantially increase the barrier height and stabilize the product, **2-NH$_2$**.

Introduction

The $(CH)_2(BH)_2$ potential energy surface is very rich in the number of structural types. On one hand, there are classical structures (Scheme 1) such as 1,2-diboretene (**2**) and diborylacetylene (**9**), while on the other hand, there are nonclassical structures such as 1,2-diboretane-3-ylidene (**3**).[1,2] Several of these structures have been characterized experimentally by using appropriate substituents in place of hydrogen.[3−9] The nonclassical bonding in these systems has attracted considerable experimental[10−19] and theoretical attention.[20−25] While the formal electron count of $(CH)_2(BH)_2$ places it in the "closo" category ($n + 1$ bonding electron pairs, where n = number of vertexes) and thus a member of the familiar $(CH)_2(BH)_n$

Scheme 1



[†] Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday.

(1) (a) Berndt, A.; Steiner, D.; Schweikart, D.; Balzereit; Menzel, M.; Winkler, H.-J.; Mehle, S.; Unverzagt, M.; Happel, T.; Schleyer, P. v. R.; Subramanian, G.; Hofmann, M. In *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society of Chemistry: Cambridge, 1997; pp 61−72. (b) Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 985.

(2) (a) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. See especially pp 49−50. (b) For an analysis of closely related systems, see: Hofmann, M.; Scheschkewitz, D.; Ghaffari, A.; Geiseler, G.; Massa, W.; Scaefer, H. H.; Berndt, A. *J. Mol. Model.* **2000**, *6*, 257.

(3) (a) Hildenbrand, M.; Pritzkow, H.; Zenneck, U.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 371. (b) Hildenbrand, M.; Pritzkow, H.; Siebert, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 759.

(4) Wehrmann, R.; Puess, C.; Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 372.

(5) Pilz, M.; Allwohn, J.; Bühl, M.; Schleyer, P. v. R.; Berndt, A. *Z. Naturforsch.* **1991**, *46B*, 1085.

(6) Kaufmann, D. E.; Boese, R.; Scheer, A. *Chem. Ber.* **1994**, *127*, 2349.

(7) Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 877.

(8) Höfner, A.; Ziegler, B.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 186.

(9) (a) Schulz, H.; Gabbert, G.; Pritzkow, H.; Siebert, W. *Chem. Ber.* **1993**, *126*, 1593. (b) Wrackmeyer, B.; Schanz, H.-J.; Hoffmann, M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1245. (c) Wrackmeyer, B.; Schanz, H.-J.; Hofmann, M.; Schleyer, P. v. R.; Boese, R. *Eur. J. Inorg. Chem.* **1999**, 533.

(10) Unverzagt, M.; Subramanian, G.; Hofmann, M.; Schleyer, P. v. R.; Berger, S.; Harms, K.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1469.

(11) Steiner, D.; Winkler, H.-J.; Balzereit, C.; Happel, T.; Hofmann, M.; Subramanian, G.; Schleyer, P. v. R.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1990.

(12) Menzel, M.; Winkler, H. J.; Ablelom, T.; Steiner, D.; Fau, S.; Frenking, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1340.

(13) Menzel, M.; Steiner, D.; Winkler, H.-J.; Schweikart, D.; Mehle, S.; Fau, S.; Frenking, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 327.

(14) Steiner, D.; Balzereit, C.; Winkler, H.-J.; Stamatis, N.; Hofmann, M.; Schleyer, P. v. R.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2303.

(15) Willerhausen, P.; Schmidt-Lukasch, G.; Kybart, C.; Allwohn, J.; Massa, W.; McKee, M. L.; Schleyer, P. v. R.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1384.

(16) Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1329.

(17) Höfner, A.; Ziegler, B.; Hunold, R.; Willershausen, P.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 594.

(18) Hunold, R.; Pilz, M.; Allwohn, J.; Stadler, M.; Massa, W.; Schleyer, P. v. R.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 781.

(19) Gunale, A.; Steiner, D.; Schweikart, D.; Pritzkow, H.; Berndt, A.; Siebert, W. *Chem. Eur. J.* **1998**, *4*, 44.

(20) Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 2589.

(21) Frenking, G.; Schaefer, H. F. *Chem. Phys. Lett.* **1984**, *109*, 521.

(22) Budzelaar, P. H. M.; Schleyer, P. v. R.; Krogh-Jespersen, K. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 825.

(23) Budzelaar, P. H. M.; Krogh-Jespersen, K.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1985**, *107*, 2773.

(24) Bühl, M.; Gauss, J.; Hofmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 12385.

(25) McKee, M. L. *Inorg. Chem.* **1999**, *38*, 321.

10.1021/ic000240f CCC: $19.00

carborane family,[26] the potential energy surface bears no similarity to other carboranes. Instead, the nonclassical structures are characterized by σ- and π-three-center-two-electron (π-3c-2e) bonds.[1,2] The π-3c-2e bond is located on a central Hückel-aromatic three-membered ring. If the σ- and π-3c-2e bonds have three atoms in common, the structure is considered "type A" (**3**, **6**), while if the σ- and π-3c-2e bonds have only two atoms in common, the structure is considered "type B" (**4**).[1,2]

The nonclassical $(CH)_2(BH)_2$ systems which have simultaneous σ- and π-3c-2e bonds have atoms (boron or carbon) with all substituents in the same hemisphere (**3**, **4**, **6**–**8**; anti-van't Hoff geometries[27]). If the "special" atom is carbon (**3**, **7**), it can be thought of as a carbene with a "reversed" electron configuration, that is, the lone pair on carbon is located in the out-of-plane π-orbital rather than the in-plane σ-orbital. In this manner, the occupied π-lone pair (on carbon or boron) participates in the π-3c-2e bond, while the empty σ-orbital participates in the σ-3c-2e bond.

Two orthogonal systems of $(4n + 2)$ electrons are called "doubly aromatic".[10] The added methylene bridge in forming **3** gives a monohomo doubly aromatic system. The diborylcarbene **7** is a π-carbene and a potential intermediate in the degenerate rearrangement of **3**.

The potential energy surface can be divided up into five different areas of stability (**1**/**2**, **3**/**7**, **4**/**6**, **5**, **9**), of which examples are known for all but **4**/**6**. Rearrangement barriers between the different groups exceed 40 kcal/mol. Ironically, the only example not known is the global minimum, cyclic (borylmethylene)borane (**4**). The purpose of this work is to compute all the $(CH)_2(BH)_2$ species and the pathways of interconversion at a consistent level of theory.

Computational Methods

All geometries were fully optimized in the given symmetry at the MP2/6-31G(d) level.[28] Vibrational frequencies were calculated to determine the nature of the stationary points and to make zero-point and heat capacity corrections. Single-point calculations were made on MP2/6-31G(d) geometries at MP4SDQT/6-31G(d) and MP2/6-311+G(d,p) to estimate relative energies at the [MP4/6-311+G(d,p)] level (brackets signify additivity approximation[29]). Zero-point corrections were made using scaled MP2/6-31G(d) frequencies (0.95 factor), while integrated heat capacities to 298 K were made with unscaled frequencies.

Molecular plots of $(CH)_2(BH)_2$ species are shown on a reaction diagram in Figures 1 and 2. Total energies (hartrees) and zero-point energies (kcal/mol) are given in Table 1 and relative energies (kcal/mol) in Table 2. Cartesian coordinates at the MP2/6-31G(d) level of all species are provided as Supporting Information.

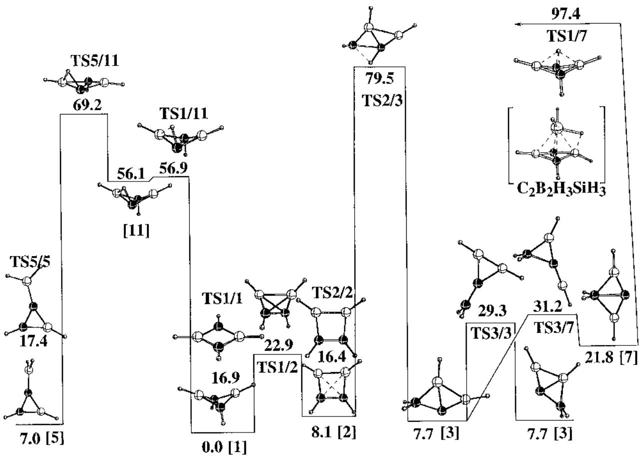


Figure 1. Reaction diagram at the [MP4/6-311+G(d,p)]//MP2/6-31G-(d)+ZPC+Cp level (at 298 K) for species on the $(CH)_2(BH)_2$ potential energy surface.

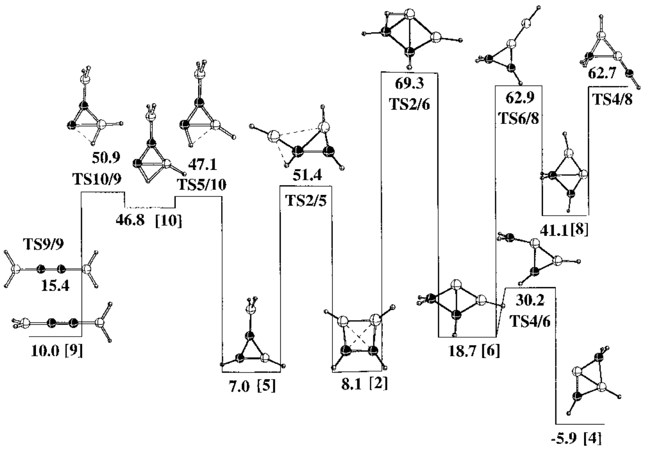


Figure 2. Reaction diagram at the [MP4/6-311+G(d,p)]//MP2/6-31G-(d)+ZPC+Cp level (at 298 K) for species on the $(CH)_2(BH)_2$ potential energy surface.

Results and Discussion

In 1985, the 3-21G geometries of many $(CH)_2(BH)_2$ isomers were calculated by Schleyer and co-workers.[23] The relative energies in their study (MP2/6-31G(d)//3-21G) are remarkably similar (Table 2) to the relative energies in the present study ([MP4/6-311+G(d,p)]//MP2/6-31G(d) plus ZPE and heat capacity corrections). The largest difference is about 5 kcal/mol.

The 1,3-isomer of diboretene (**1**) is calculated to be 8.1 kcal/mol more stable than the 1,2-isomer (**2**). Both isomers can be considered as distorted tetrahedra. The dihedral angles around the perimeters of **1** and **2** are very similar (39.7° and 39.1°, respectively), as are the averages of the six C–C, B–B, and C–B distances (1.661 and 1.685 Å, respectively). The least-motion reaction path for interconverting **1** and **2** is a diamond-square-diamond (DSD) step.[30] However, the DSD pathway is blocked by a HOMO–LUMO crossing similar in nature to that found in the rearrangement of $(CH)_2(BH)_3$ and $(CH)_2(BH)_4$.[31,32]

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(26) Grimes, R. N. *Carboranes*; Academic Press: New York, 1970.

(27) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian: Pittsburgh, PA, 1998.

(29) (a) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673. (b) Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497. (c) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1985**, *24*, 762.

(30) McKee, M. L. Fluxional Process in Boranes and Carboranes. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Kollmann, P. A., Clark, T., Schaefer, H. F., Gasteiger, J., Schreiner, P. R., Eds.; Wiley-VCH: New York, 1998.

(31) (a) Grimarc, B. M.; Ott, J. J. *Inorg. Chem.* **1986**, *25*, 83. (b) Grimarc, B. M.; Ott, J. J. *Inorg. Chem.* **1986**, *25*, 2708.

(32) (a) McKee, M. L. *THEOCHEM* **1988**, *168*, 191. (b) McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 5317. (c) McKee, M. L. Mechanistic Patterns in Carborane Reactions. In *The Borane, Carborane and Carbocation Continuum*; Casanova, J., Ed.; Wiley: New York, 1998.

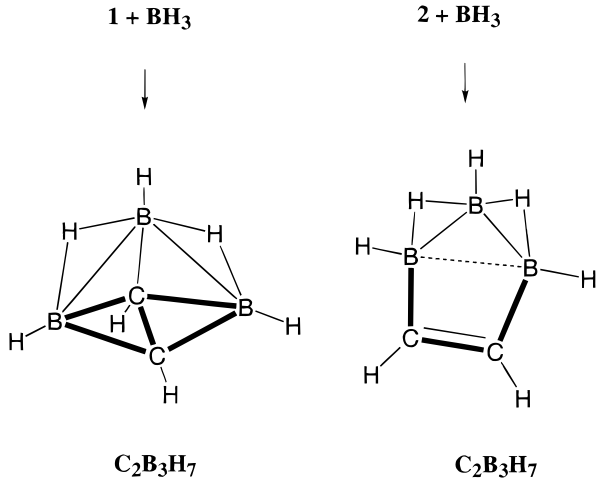
Table 1. Absolute Energies (hartrees), Zero-Point Energies (kcal/mol), and Heat Capacity Corrections to 298 K (kcal/mol)

	PG	MP2/a	MP4/a	MP2/b	ZPE(NIF)[a]	cp corr (298 K)
1	C_{2v}	−127.76989	−127.81904	−127.84260	35.63(0)	3.06
2	C_2	−127.75609	−127.80688	−127.82812	35.53(0)	3.14
3	C_s	−127.76020	−127.80866	−127.83147	35.86(0)	3.18
4	C_s	−127.77908	−127.82901	−127.85313	36.77(0)	3.10
5	C_s	−127.75849	−127.80876	−127.82856	34.07(0)	3.57
6	C_s	−127.73915	−127.78971	−127.81314	36.67(0)	3.12
7	C_{2v}	−127.73286	−127.78322	−127.80693	35.47(0)	3.34
8	C_s	−127.69763	−127.75095	−127.77432	36.36(0)	3.27
9	D_{2h}	−127.74924	−127.80260	−127.81941	32.59(0)	4.06
10	C_s	−127.68494	−127.73689	−127.76171	32.62(0)	3.65
11	C_1	−127.66340	−127.71514	−127.74717	32.89(0)	3.50
TS1/1	D_{2h}	−127.73646	−127.79049	−127.80995	35.31(1)	2.81
TS2/2	C_{2v}	−127.73846	−127.79126	−127.81182	35.26(1)	2.83
TS3/3	C_{2v}	−127.71601	−127.76959	−127.78926	33.79(1)	3.36
TS5/5	C_s	−127.74106	−127.79135	−127.81136	33.82(1)	3.24
TS1/2	C_2	−127.73232	−127.77995	−127.80590	34.70(1)	2.96
TS2/3	C_1	−127.62378	−127.67732	−127.70581	31.51(1)	3.49
TS3/7	C_s	−127.71350	−127.76507	−127.78916	34.55(1)	3.23
TS1/7	C_s	−127.59092	−127.64294	−127.67765	30.90(1)	3.25
TS6/8	C_s	−127.65572	−127.71298	−127.73430	35.32(1)	3.22
TS4/6	C_s	−127.71269	−127.76653	−127.78908	35.02(1)	3.14
TS4/8	C_s	−127.65000	−127.70900	−127.73167	34.45(1)	3.50
TS1/11	C_1	−127.66271	−127.71403	−127.74551	32.69(1)	3.12
TS5/11	C_1	−127.64565	−127.69841	−127.72392	32.20(1)	3.26
TS2/6	C_1	−127.64497	−127.69841	−127.72437	33.34(1)	3.02
TS2/5	C_1	−127.67239	−127.72416	−127.75264	32.23(1)	2.94
TS5/10	C_s	−127.68398	−127.73501	−127.76065	31.73(1)	3.68
TS10/9	C_s	−127.67496	−127.73038	−127.74940	31.23(1)	3.63
TS9/9	D_{2h}	−127.74168	−127.79285	−127.81174	31.97(1)	3.85
1-NH$_2$	C_{2v}	−238.25497	−238.32337	−238.40947	59.51(0)	4.71
2-NH$_2$	C_2	−238.25096	−238.32349	−238.40494	59.88(0)	4.75
TS1/1-NH$_2$	D_{2h}	−238.21961	−238.29410	−238.37547	58.33(1)	4.68
TS2/2-NH$_2$	C_{2v}	−238.25092	−238.32355	−238.40485	59.79(1)	4.24
TS1/2-NH$_2$	C_2	−238.19975	−238.26661	−238.35525	58.00(1)	4.85

[a] Zero-point energy with number on imaginary frequencies in parentheses.

The reaction path interconverting **1** and **2** maintains a C_2 axis. The transition state (**TS1/2**) resembles a less distorted tetrahedron than either **1** or **2**, with C−C, B−B, and C−B distances of 1.588, 1.896, and 1.402/1.774 Å, respectively. The activation enthalpy is 22.9 kcal/mol in the forward direction (**1** → **2**) and 14.8 kcal/mol in the reverse direction. In comparison, the inversion barriers are 16.9 kcal/mol for **1** through transition state **TS1/1** and 8.3 kcal/mol for **2** through transition state **TS2/2**. It is interesting to note that BH_3 adds without an activation barrier to **1** in forming one isomer of $C_2B_3H_7$ (see **1** + BH_3), while BH_3 adds to **2** without barrier in forming another isomer of $C_2B_3H_7$ (see **2** + BH_3).[33] These two $C_2B_3H_7$ isomers do not readily interconvert.[33]

The 1,2-diboretane-3-ylidene isomer (**3**) has attracted attention due to its orthogonal aromatic systems and unusual bonding.[1,21,22] It is 0.4 kcal/mol more stable than **2** but separated by a 71.8 kcal/mol barrier. The barrier is unusually high for several reasons. First, in **3**, there are two π-type orbitals, the π-3c-2e bond and the π-type combination of the $C-H_2$ σ-bonds, while in **2**, there is one C=C π-bond. Second, the π-3c-2e bond in **3** is converted into a C=C π-bond in **2**, which means that aromatic stabilization in **3** is lost. Third, hydrogen migrations between carbon atoms are generally unfavorable (relative to hydrogen migrations between boron atoms). Indeed, the C−C bond becomes very long in the transition state (1.790 Å) to permit the in-plane migration of the hydrogen atom to what has become essentially a carbenic center.



It is difficult to rationalize the observation made by Berndt[3] that a derivative of **3** thermally rearranges to **2**. There is an alternative route, **3** → **2** through **7** and **1** (i.e., **3** → **7** → **1** → **2**). However, that pathway is blocked by an even higher activation barrier **7** → **1** (**7** → **TS1/7**, 75.6 kcal/mol). In the system observed by Berndt, a silyl group rather than a hydrogen in the parent system migrates between carbons. In this pathway, the activation barrier is substatially reduced when the migrating hydrogen is replaced by a SiH_3 group. The enthalpy barrier (**3** → **TS1/7**) is reduced by 34.7 kcal/mol when SiH_3 replaces H (or 35.4 kcal/mol when both CH_2 hydrogens are replaced by

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(33) McKee, M. L. Unpublished work.

Table 2. Relative Energies (kcal/mol) of $(CH)_2(BH)_2$ Species

	MP2/a	MP4/a	MP2/b	[MP4/b] energy	[MP4/b] +ZPC	[MP4/b] +Cp	MP2/ 6-31G(d)[a]// 3-21G
1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	8.6	7.6	9.1	8.1	8.0	8.1	
3	6.1	6.5	7.0	7.4	7.6	7.7	7.5
4	−5.8	−6.2	−6.6	−7.0	−5.9	−5.9	−5.7
5	7.2	6.4	8.8	8.0	6.5	7.0	6.1
6	19.3	18.4	18.5	17.6	18.6	18.7	19.3
7	23.2	22.5	22.4	21.7	21.5	21.8	23.9
8	45.3	42.7	42.8	40.2	40.9	41.1	45.9
9	13.0	10.3	14.6	11.9	9.0	10.0	12.1
10	53.3	51.5	50.8	49.0	46.2	46.8	
11	66.8	65.2	59.9	58.3	55.7	56.1	
TS1/1	21.0	17.9	20.5	17.4	17.1	16.9	19.7
TS2/2	19.7	17.4	19.3	17.0	16.6	16.4	18.8
TS3/3	33.8	31.0	33.5	30.7	29.0	29.3	33.1
TS5/5	18.1	17.4	19.6	18.9	17.2	17.4	16.9
TS1/2	23.6	24.5	23.0	23.9	23.0	22.9	24.5
TS2/3	91.7	88.9	85.8	83.0	79.1	79.5	
TS3/7	35.4	33.9	33.5	32.0	31.0	31.2	
TS1/7	112.3	110.5	103.5	101.7	97.2	97.4	
TS6/8	71.6	66.6	68.0	63.0	62.7	62.9	
TS4/6	35.9	33.0	33.6	30.7	30.1	30.2	
TS4/8	75.2	69.0	69.6	63.4	62.3	62.7	
TS1/11	67.2	65.9	60.9	59.6	56.8	56.9	
TS5/11	78.0	75.7	74.5	72.2	69.0	69.2	
TS2/6	78.4	75.7	74.2	71.5	69.3	69.3	
TS2/5	61.2	59.5	56.4	54.7	51.5	51.4	
TS5/10	53.9	52.7	51.4	50.2	46.5	47.1	
TS10/9	59.6	55.6	58.5	54.5	50.3	50.9	
TS9/9	17.7	16.4	19.4	18.1	14.6	15.4	17.7
1-NH$_2$	0.0	0.0	0.0	0.0	0.0	0.0	
2-NH$_2$	2.5	−0.1	2.8	0.2	0.6	0.6	
TS1/1- NH$_2$	22.2	18.4	21.3	17.5	16.4	16.4	
TS2/2- NH$_2$	2.5	−0.1	2.9	0.3	0.6	0.1	
TS1/2- NH$_2$	34.6	35.6	34.0	35.0	33.6	33.7	

[a] Ref 23.

SiH_3 groups; see Figures 3 and 4). The enthalpy lowering is due to the smaller bond strength of a C−Si bond compared to a C−H bond and to the fact that hydrogen cannot effectively bridge the two carbons in the transition state. An additional factor relevant to the migration of the SiH_3 group (but not a SiR_3 group) is that one of the hydrogens of the silyl group bridges to boron in the transition state (**TS1/7-SiH$_3$**; SiH/BH 1.621/1.322 Å).

A derivative of **3**, where $SiMe_3$ groups replace CH hydrogens and *t*-Bu groups replace BH hydrogens, is known to undergo a degenerate rearrangement which exchanges the boron atoms with an experimental barrier of 11.4 kcal/mol.[7] The rearrangement has been proposed[22] to occur via transition state **TS3/3** or intermediate **7**. In the former pathway with a 29.3 kcal/mol barrier, a CH_2 group swings between two equivalent bridging C/B positions. In the latter pathway with a 31.2 kcal/mol barrier, a BH group swings between a C/B position in **3** and a C/C position in **7**. Calculations by Schleyer and coworkers[23] show that SiH_3 and CH_3 substituents in **3** lower the rearrangement barrier via intermediate **7**.

The formation of **5** can take place by reaction from **1** or **2**. From **1**, a shallow minimum (**11**) is reached where a C−H terminal bond has been transformed into a C−H−B bridge. Continued lengthening of the C−H interaction breaks the C−H−B bridge to form the BH_2 group of **5**. The overall barrier of **1** → **5** is 69.2 kcal/mol. A pathway with a lower overall barrier, **1** → **2** → **5** (51.4 kcal/mol), was found. The **TS2/5** is characterized by concerted B−B bond breaking and the formation of a B−H bond. The BH_2 group in **5** is perpendicular to the three-membered ring to allow more effective conjugation, as pointed out by Schleyer and coworkers. The rotational barrier is calculated to be 10.4 kcal/mol.

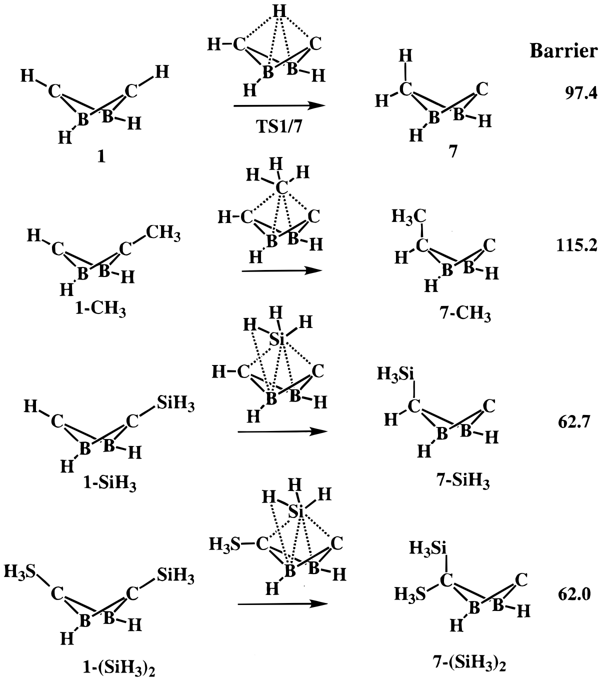

Figure 3. Comparison of activation enthalpies ([MP4/6-311+G(d,p)]//MP2/6-31G(d)+ZPC+Cp level (at 298 K)) for the reaction **1** → **7** and its derivatives. The barrier is substantially reduced when the migration group is SiH_3 rather than H or CH_3. The effect of the nonmigrating substituent (H or SiH_3) on the barrier is small.

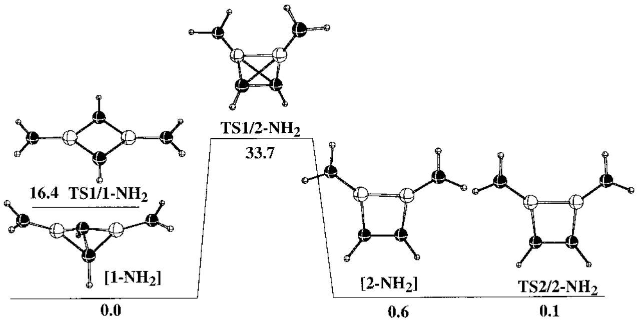

Figure 4. Reaction diagram at the [MP4/6-311+G(d,p)]//MP2/6-31G-(d)+ZPC+Cp level (at 298 K) for species on the $(CH)_2(BNH_2)_2$ potential energy surface.

The type A system **6** can be formed from **2** with an activation barrier of 61.2 kcal/mol. In the transition state **TS2/6**, a hydrogen is migrating from boron to carbon. The intermediate **6** has a very low barrier (11.5 kcal/mol) in forming **4**, the $(CH)_2(BH)_2$ global minimum. There is an alternative pathway through **TS6/8** for **6** to form **8**, whose structure is similar to that of **7** with the interchange of carbon and boron. In turn, **8** can form **4** through **TS4/8** which has an activation barrier of 21.6 kcal/mol.

The lowest-energy pathway to **9** is from **5**. The first step is the migration of hydrogen from a terminal C−H bond to a C−H−B bridge in the intermediate **10**. The second step is the formation of a BH_2 group of **9** from the C−H−B bridge of **10**. The overall activation enthalpy from **5** → **9** is 43.9 kcal/mol.

$(CH)_2(BNH_2)_2$ Rearrangements. It is well known that replacing hydrogen on boron with substituents which are π-electron donors can stabilize classical structures.[34,35] For

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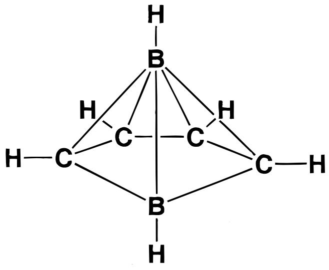
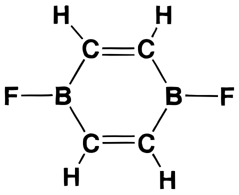
(34) Budzelaar, P. H. M.; Kos, A. J.; Clark, T.; Schleyer, P. v. R. *Organometallics* **1985**, *4*, 429.

example, $C_4B_2H_6$ is known to have the nonclassical structure, while replacing the BH hydrogens with fluorines gives the classical structure.[33] Since derivatives of both **1** and **2** are known with BH hydrogens replaced with NR_2 groups,[3,5,6] it was of interest to see how NH_2 would affect the potential energy surface (PES). While **2** is 8.1 kcal/mol less stable than **1** on the $(CH)_2(BH)_2$ PES, the difference is reduced to only 0.6 kcal/mol on the $(CH_2)(BNH_2)_2$ PES. On the other hand, the barrier height between **1-NH₂** and **2-NH₂** has increased 10.8 kcal/mol relative to the parent system. It is this increase in the activation barrier which allows both NH_2-substituted isomers to be isolated. The transition state **TS1/2-NH₂** closely resembles the nonclassical closo tetrahedron, which is expected to be destabilized relative to the reactant and product by NH_2 substitution. While both **2** and **2-NH₂** have nonplanar geometries, the barrier to planarity is greatly reduced for the latter. In fact, after zero-point and heat capacity corrections have been included, the planar transition state (**TS2/2-NH₂**) is actually 0.5 kcal/mol lower in enthalpy than **2-NH₂**. For **1-NH₂**, NH_2 substitution has little affect on the barrier to planarity compared to in the parent system (16.4, **1-NH₂** kcal/mol; 16.9 kcal/mol, **1**).



$C_4B_2H_6$



$C_4B_2F_2H_4$

Conclusions

A thorough investigation of the $(CH)_2(BH)_2$ potential energy surface has revealed that a number of isomers are separated by high barriers of activation, which explains why such a variety of structures have have been found for derivatives of $(CH)_2(BH)_2$. In contrast, most other members of the carborane family, $(CH)_2(BH)_n$, have one or two (at the most three) known isomers. For most derivatives of carboranes, the exo substituents are believed to exert an electronic or steric effect, which may lower rearrangement barriers. However, the silyl substitutent of the known derivative of the 1,2-diboretane-3-ylidene isomer (**3**) takes a different rearrangement pathway compared to the parent due to the greater ability of silyl (compared to hydrogen) to span the opposite positions in the diamond transition state.

The cyclic (borylmethylene)borane isomer (**4**) is the global minimum of the $(CH)_2(BH)_2$ PES. The methylene group attached to the bare boron atom is more stable bridging the C−B bond in **6** than the B−B bond in **4**.

When NH_2 groups replace BH hydrogens in $(CH)_2(BH)_2$, the classical structure is stabilized more than the nonclassical. Thus, classical **2-NH₂** (1,2-diamino-1,2-diboretene) is predicted to be planar and have nearly the same energy as the more nonclassical **1-NH₂** (1,3-diamino-1,3-diboretene). Furthermore, the transition state between **1-NH₂** and **2-NH₂**, which resembles a tetrahedron, is destabilized by the NH_2 substituents.

Acknowledgment. Computer time was provided by the Alabama Supercomputer Network. The author thanks Sun Microsystems Computer Corporation for an academic equipment grant and Professor Armin Berndt for helpful conversations and for suggesting **TS1/7**.

Supporting Information Available: A table (Table S1) listing Cartesian coordinates for relevant structures optimized at the MP2/6-31G(d) level This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Camp, R. N.; Marynick, D. S.; Graham, G. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6781.