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Carboranes and Baskets from Reaction of B_4H_{10} with Allene

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The reaction of the boron hydride B_4H_{10} with allene was studied at the CCSD(T)/6-311+G(d)//MP2/6-31G(d) level. The mechanism is surprisingly complex with 44 transition states and several branching points located. The four carboranes and one basket that have been observed experimentally are all connected by pathways that have very similar free energies of activation. In addition, two new structures, a basket (2,4-($CH_2CH_2CH_2$)B_4H_8, **5a**) and a "classical" structure (1,4-(Me_2C)bisdiborane, **7**), which might be obtained from the B_4H_{10} + C_3H_4 reaction under the right conditions (hot/cold, quenched, etc.) have been identified. The first branch point in the reaction is the competition between H_2 elimination from B_4H_{10} (ΔG(298 K) = 32.2 kcal/mol) and the hydroboration of allene by B_4H_{10} (ΔG(298 K) = 31.3 kcal/mol). The next branch point in the hydroboration mechanism controls the formation of 2,4-($MeCHCH_2$)B_4H_8 (**1**) (ΔG(298 K) = 31.5 kcal/mol) and *arachno*-1,2/*arachno*-1,3-Me_2-1-CB_4H_7 (**8** and **8a**) (ΔG(298 K) = 34.3 kcal/mol). Another branch point in the H_2-elimination mechanism controls the formation of 1-Me-2,5-μ-CH_2-1-CB_4H_7 (**29**) (ΔG(298 K) = 0.1 kcal/mol) and 2,5-μ-CHMe-1-CB_4H_7 (**25/26**) (ΔG(298 K) = 7.3 kcal/mol). Formation of 2-Me-2,3-$C_2B_4H_7$, a carborane observed in the reaction of methylacetylene with B_4H_{10}, is calculated to be blocked by a high barrier for H_2 elimination. All free energies are relative to B_4H_{10} + allene. An interesting reaction step discovered is the "reverse hydroboration step" in which a hydrogen atom is transferred from carbon back to boron, which allows a CH hydrogen to shuttle between the terminal and central carbon of allene.

Introduction

It is well-known that alkynes, alkenes, and enynes react in the gas phase with boranes such as B_4H_{10}, often producing a surprising mixture of compounds[1−8] in which carbon is incorporated into the clusters to form carboranes and/or a basketlike compound.[9−13] Two hydrocarbon isomers, allene and methylactylene, react with B_4H_{10} to generate six observeable products depending on the reaction conditions (Scheme 1). Under "hot/cold" conditions with allene, the basket compound 2,4-($MeCHCH_2$)B_4H_8 (**1**) is formed, as well as four carboranes. On the other hand, methylacetylene forms two of the same carboranes, as well as 2-Me-2,3-$C_2B_4H_7$ (**34**), a product not detected in the allene + B_4H_{10} reaction.

The reaction of boron hydrides with alkynes and alkenes have complex reaction mechanisms with a number of intermediates of similar energy. In contrast to hydrocarbons, the bonding in the boron hydrides is electron deficient where several bonding patterns may have similar stability. There are many examples of "nonclassical" versus "classical" isomers where the former structures have a greater number of three-center two-electron bonds (3c-2e) while the latter structures have a greater number of 2c-2e bonds with a vacant

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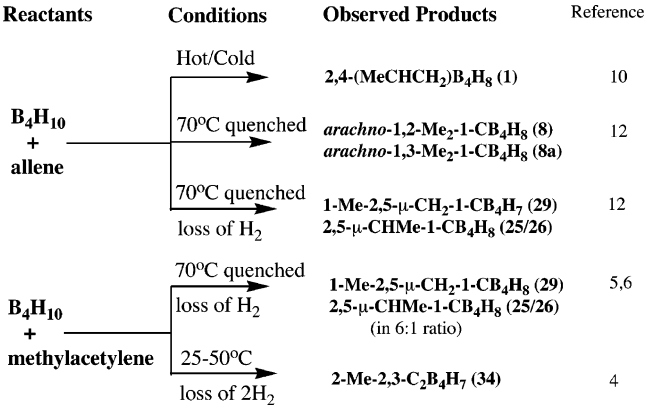
Scheme 1



orbital on boron. Several mechanistic steps have been identified, the most notable of which is the diamond−square−diamond (DSD) step[14,15] where two fused diamonds go through a square transition state to form products with an interchange of bonds. Another well-known step is the hydroboration (HB) step in which an empty orbital on boron forms a π complex with a C−C double or triple bond followed by migration of the BH hydrogen to one carbon and the boron to the other carbon. It is known that acetylene adds to boron hydrides to form carboranes in which the C−C triple bond can be ultimately broken. How this is achieved is not completely understood, but theoretical calculations are making a contribution.[16−21] In a series of two papers,[16,17] one of the authors computed the reaction of acetylene with B_4H_{10} with the assumption that the first step of the reaction was the decomposition of B_4H_{10} to BH_3, B_3H_7, and B_4H_8 (eqs 1−3). In a subsequent paper[18] the addition of ethylene to B_4H_{10} was studied where a path to the basket 2,4-$(CH_2CH_2)B_4H_8$ was identified.

$$HC{\equiv}CH + BH_3 \rightarrow H_2C{=}CHBH_2 \quad (1)$$

$$HC{\equiv}CH + B_3H_7 \rightarrow C_2B_3H_9, C_2B_3H_7, C_2B_3H_5 \quad (2)$$

$$HC{\equiv}CH + B_4H_8 \rightarrow C_2B_4H_{10}, C_2B_4H_8, C_2B_4H_6 \quad (3)$$

The rate-determining step in the reaction of B_4H_{10} with many unsaturated hydrocarbons involves the elimination of H_2 to give B_4H_8 as the reactive species (eq 5).[22−26]

$$B_4H_{10} + H_2C{=}C{=}CH_2 \rightarrow C_3B_4H_{14} \quad (4)$$

$$B_4H_{10} \rightarrow B_4H_8 + H_2 \quad (5)$$

$$B_4H_8 + H_2C{=}C{=}CH_2 \rightarrow C_3B_4H_{12} \quad (6)$$

A study by Fox et al.[12] demonstrated that the formation of $C_3B_4H_{14}$ according to eq 4 and the formation of $C_3B_4H_{12}$ according to eqs 5 and 6 may be competitive with each other. The latter carborane, $C_3B_4H_{12}$, was first produced by Greatrex et al.[4] from the reaction between B_4H_{10} and propyne under hot/cold conditions. However, their proposed structure, based on NMR evidence, was subsequently shown by Fox et al.[5] to be incorrect.

Methods

Since the MP2/6-31G(d) method has provided accurate geometries for boranes and carboranes,[27] all geometries were fully optimized at the MP2/6-31G(d) level. Vibrational frequencies were calculated at that level to make zero-point energy and thermal corrections and single-point calculations were made at the CCSD(T)/6-311+G(d) level to give more reliable energies. All electronic structure calculations have used the Gaussian 03 program.[28] Imaginary frequencies for transition states were animated by using graphical program MolDen[29] to ensure that the motion of the transition vector was appropriate for converting reactants to products. In addition, intrinsic reaction coordinate (IRC) calculations have been performed on most transition states to verify which minima are connected to the transition state. In the discussion below, all free energies denoted by ΔG at 298 K are relative to B_4H_{10} plus allene while free energies of activation denoted by $\Delta G^{\ddagger}$ at 298 K are relative to an individual reaction step.

Results and Discussions

In the reaction of B_4H_{10} with allene, some of the observed products do not involve the initial loss of H_2. We considered two initial hydroboration steps (Figures 1 and 2), one from B_4H_{10} (**2→TS2/3→3**), and another involving an activated form of B_4H_{10} (**2→TS2/2a→2a→TS2a/3→3**). The activated form of B_4H_{10} has a five-coordinate boron center (**2a**) and has been implicated in the initial hydroboration step of B_4H_{10}

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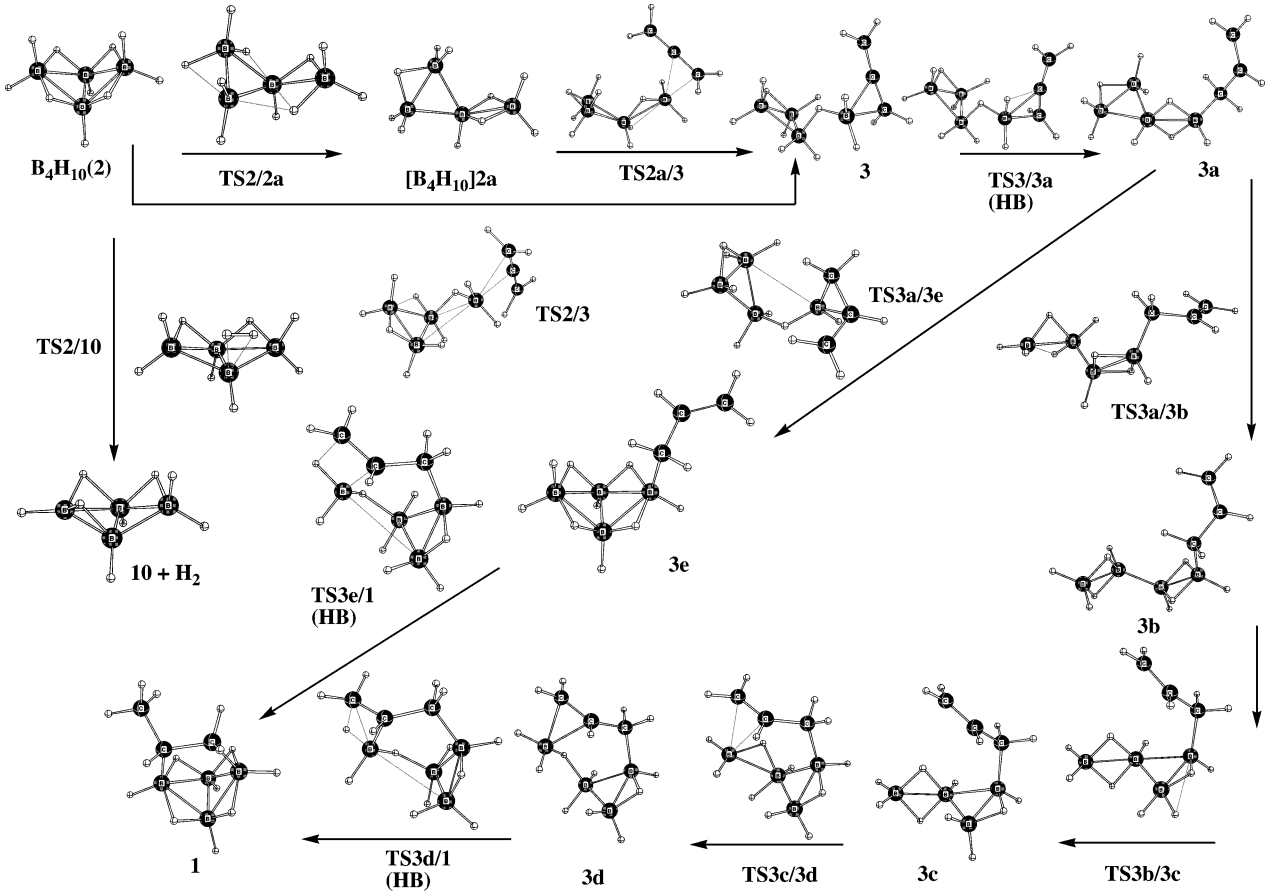

Figure 1. Stationary points along the reaction pathway for formation of basket compound **1**, MP2/6-31G(d) optimized. "HB" indicates a hydrobortion transition state.

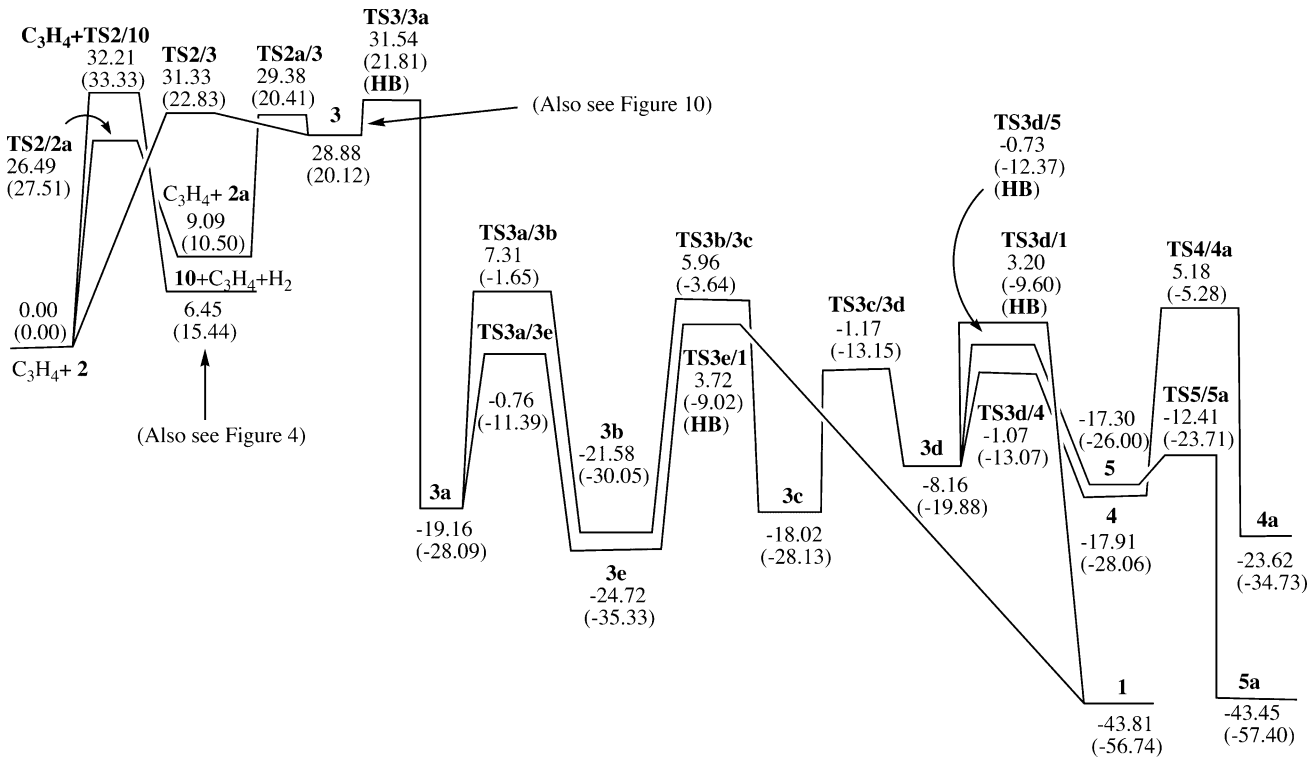

Figure 2. Schematic reaction profile for reaction of B_4H_8 with allene at the CCSD(T)/6-311+G(d)//MP2/6-31G(d) level. Relative free energies (enthalpies in parentheses) are given in kcal/mol at 298 K relative to allene + B_4H_{10}.

Table 1. Relative Energies, Enthalpies, and Free Energies (kcal/mol) of Various Species

	relative ΔH(298 K)[a]		relative ΔG(298 K)[a]
	MP2/a	CCSD(T)/b//MP2/a	CCSD(T)/b//MP2/a
allene + B_4H_{10} (**2**)	0.00	0.00	0.00
allene + **TS2/2a**	31.37	27.51	26.49
allene + **2a**	12.83	10.50	9.09
TS2/10	40.46	33.33	32.21
B_4H_8(**10**) + C_3H_4+H_2	16.64	15.44	6.45
TS2/3	24.90	22.83	31.33
TS2a/3	21.74	20.41	29.38
3	20.95	20.12	28.88
TS3/3a	21.71	21.81	31.54
3a	−27.21	−28.10	−19.16
TS3a/3e	−11.80	−11.39	−0.76
3e	−37.19	−35.33	−24.72
TS3e/1	−16.82	−9.02	3.72
TS3a/3b	0.73	−1.65	7.31
3b	−28.91	−30.05	−21.58
TS3b/3c	−1.83	−3.64	5.96
3c	−27.94	−28.13	−18.02
TS3c/3d	−13.81	−13.15	−1.17
3d	−20.84	−19.88	−8.16
TS3d/1	−12.41	−9.60	3.20
1	−60.19	−56.74	−43.81
TS3d/4	−13.73	−13.07	−1.07
4	−27.87	−28.06	−17.91
TS4/4a	−3.76	−5.28	5.18
4a	−36.75	−34.73	−23.62
TS3d/5	−13.68	−12.37	−0.73
5	−26.83	−26.00	−17.30
TS5/5a	−23.36	−23.71	−12.41
5a	−61.26	−57.40	−43.45
TS3/6	25.18	24.76	34.34
6	−28.88	−28.58	−19.00
TS6/12	−10.28	−11.22	−0.84
12	−40.38	−37.60	−26.75
TS6/6a	−8.63	−9.46	1.94
6a	−17.93	−17.80	−6.22
TS6a/7	−12.37	−11.10	0.78
7	−52.23	−51.97	−39.42
TS7/7a	−19.61	−20.47	−8.51
7a	−32.58	−29.61	−17.58
TS7a/8	−1.44	1.25	14.04
1,2-Me_2-1-CB_4H_8 (**8**)	−72.05	−65.50	−54.04
TS8/8a	−65.58	−59.97	−48.38
1,2-Me_2-1-CB_4H_8 (**8a**)	−73.77	−67.48	−55.97

[a] Basis set "a" is 6-31G(d); basis set "b" is 6-311+G(d).

Table 2. Relative Enthalpies and Free Energies (kcal/mol) of Various Species

	relative ΔH(298 K)[a]		relative ΔG(298 K)[a]
	MP2/a	CCSD(T)/b//MP2/a	CCSD(T)/b//MP2/a
allene + B_4H_8 (**10**)	16.64	15.44	6.45
TS10/11	26.24	24.61	25.91
11	−5.69	1.34	4.42
TS11/12	23.54	31.72	35.09
12	−43.81	−34.99	−31.20
TS12/13	−26.01	−19.24	−14.87
13	−39.54	−33.53	−29.31
TS13/14	−13.84	−11.62	−7.41
14	−14.19	−11.33	−7.51
TS14/15	−0.88	2.79	7.24
15	−9.11	−5.21	−1.33
TS15/16	−0.14	3.11	7.27
16	−10.52	−6.85	−3.06
TS16/17	−9.59	−7.08	−3.12
17	−26.47	−21.95	−18.50
TS17/18	−4.87	−0.61	2.81
18	−23.99	−18.38	−15.43
TS18/19	−22.08	−17.95	−14.72
19	−28.84	−25.50	−22.59
TS19/20	−21.19	−17.36	−14.39
20	−31.99	−25.50	−22.25
TS20/21	−15.08	−8.47	−4.78
21	−31.79	−25.87	−22.50
TS21/22	−29.50	−23.04	−19.05
22	−42.81	−35.31	−31.15
TS22/23	−23.40	−16.69	−12.31
23	−26.07	−21.60	−17.43
TS23/24	−5.99	−2.72	1.22
24	−11.39	−3.91	−0.89
TS24/25	−2.42	6.61	10.63
25	−61.39	−53.41	−49.06
TS25/26	−13.15	−5.40	−2.82
26	−60.69	−52.58	−48.33
TS13/27	−3.20	−3.99	0.06
27	−34.74	−32.14	−28.69
TS27/28	−27.57	−23.79	−20.80
28	−42.79	−39.99	−37.96
TS28/29	−25.16	−21.80	−18.82
29	−63.64	−55.30	−51.27
TS13/30	16.63	18.39	21.47
30	−1.97	4.21	−1.07
TS30/31	13.39	16.08	10.41
31	7.40	9.95	3.62
TS31/32	8.59	10.90	5.05
32	6.50	11.95	5.66
TS32/33	5.83	11.39	6.06
33	−39.93	−29.48	−33.87
TS33/34	−38.86	−27.48	−31.92
34	−64.22	−52.49	−56.82

[a] Basis set "a" is 6-31G(d); basis set "b" is 6-311+G(d).

with ethylene[18] and in the butterfly to bisboranyl rearrangement in B_4H_{10}.[30] The two transition states, **TS2/3** and **TS2a/3**, resemble each other very strongly with the latter slightly lower in free energy (31.3 vs 29.4 kcal/mol). Both steps converge at structure **3** which has a small free energy barrier ($\Delta G^{\ddagger}$ = 2.7 kcal/mol) to form **3a**, a propene-substituted version of **2a**. Structure **3a** leads to the basket structure **1** in either two steps (**3a→3e→1**) or four steps (**3a→3b→3c→3d→1**). The highest intervening barrier in the two-step path is **TS3e/1** (ΔG = 3.7 kcal/mol), while it is **TS3a/3b** (ΔG = 7.3 kcal/mol) in the four-step path. We note that **3b** is a derivative of the bis(diboranyl) structure of B_4H_{10}.[30,31]

The initial hydroboration steps (Figures 1 and 2; **2→TS2/2a→2a→TS2a/3→3→TS3/3a→3a**) compete with the H_2 elimination step (**2→TS2/10→10**+H_2); the former has a free energy of 31.5 kcal/mol (**TS3/3a**) and the latter 32.2 kcal/mol (**TS2/10**). The B_4H_8 species **10** with three BHB bridges adds to a double bond of allene to form **11**, followed by a hydroboration step (Figures 3 and 4; **TS11/12**). The activation free energy for this step is high ($\Delta G^{\ddagger}$ = 30.7 kcal/mol). A pentagonal pyramid (**13**) is formed next with adjacent carbons in the base, much like the framework of the well-known 2,3-$C_2B_4H_8$ isomer.[32] This intermediate will serve as the starting point (Figures 5 and 6) for formation of 2-Me-2,3-$C_2B_4H_7$ (**34**), a product observed[4] in the reaction of methylacetylene with B_4H_{10}, but not in the reaction of allene with B_4H_{10}.[12]

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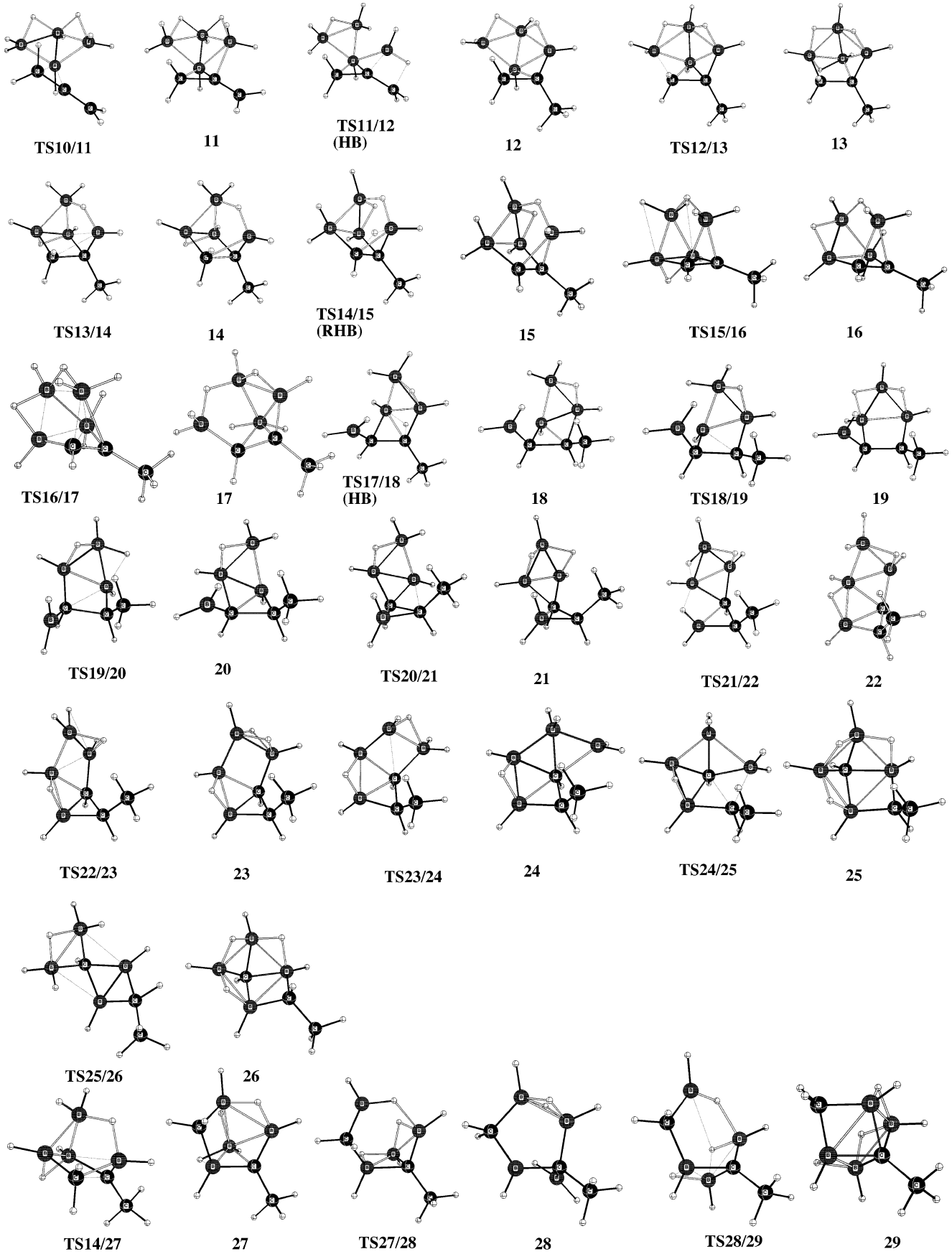

Figure 3. Stationary points along for the formation of *arachno*-carbapentaborane (**25**/**26** and **29**), MP2/6-31G(d) optimized.

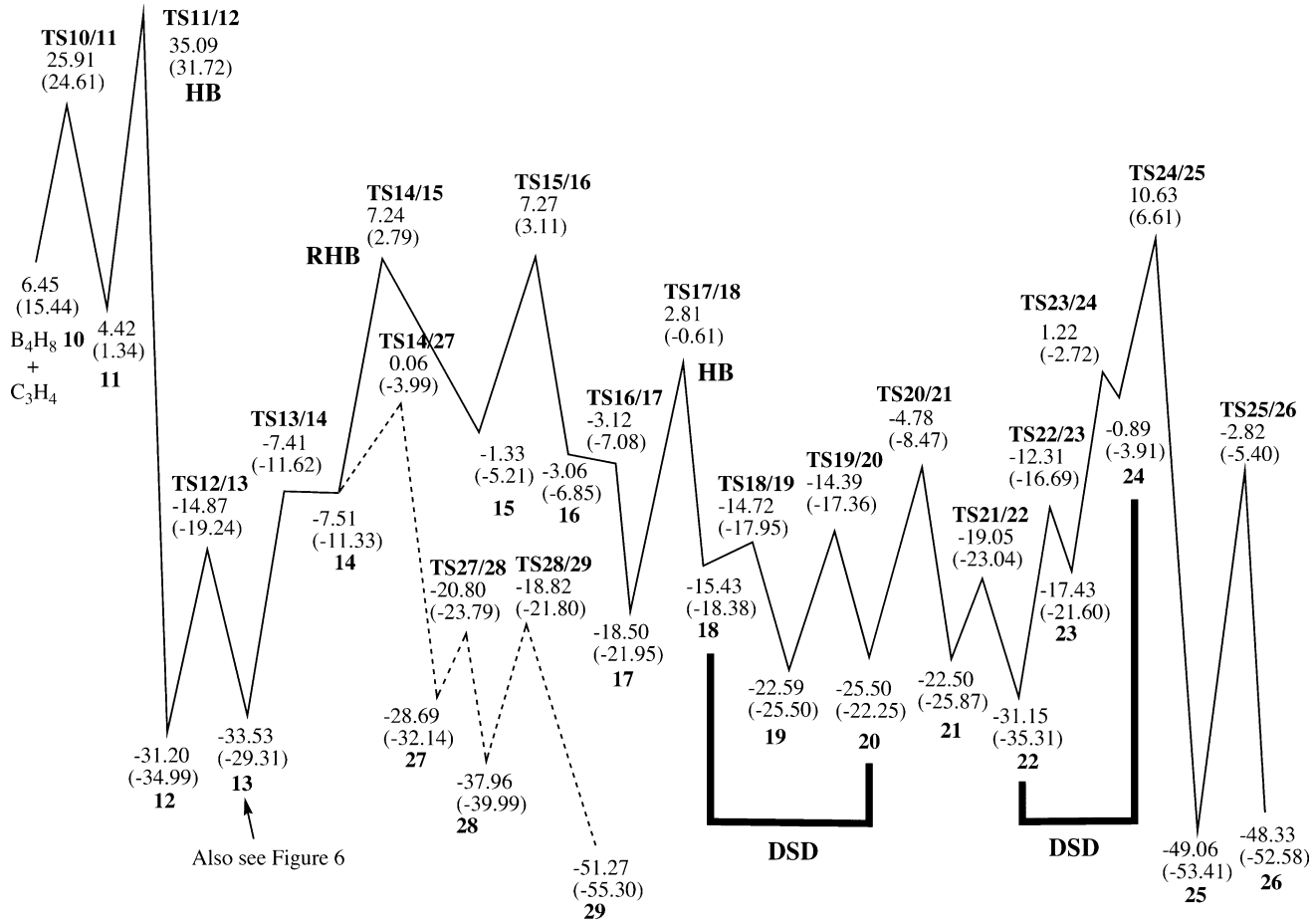

Figure 4. Schematic reaction profile for formation of **25/26** and **29** at the CCSD(T)/6-311+G(d)/MP2/6-31G(d) level. Relative free energies (enthalpies in parentheses) are given in kcal/mol at 298 K relative to allene + B_4H_{10}. All intermediates and transition states contain a H_2 molecule.

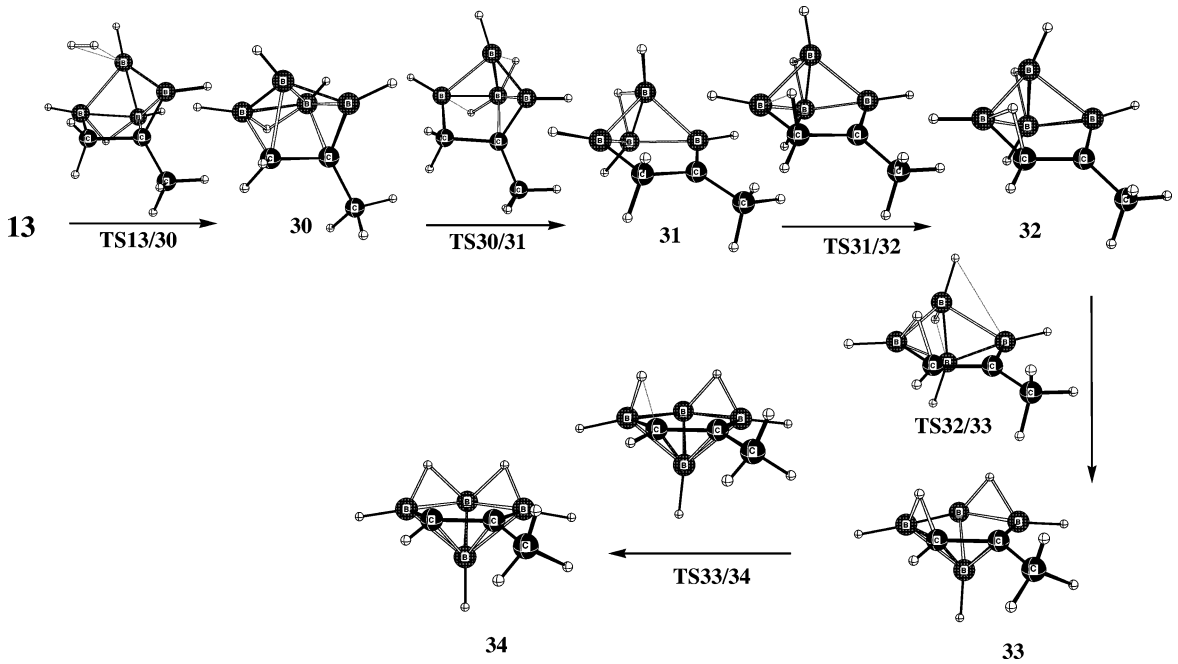

Figure 5. Stationary points along for the formation of 2-Me-2,3-$C_2B_4H_7$ (**34**), MP2/6-31G(d) optimized.

The reaction of **13→[TS13/14→14]**[33]**→TS14/15→15** (Figure 4; $\Delta G^{\ddagger} = 40.8$ kcal/mol) is an example of a reverse hydroboration (RHB) step where a CH hydrogen is transferred to boron. The reaction **15→TS15/16→16** is a synchronous conversion of a BHB→BH and a BH→BHB involving two hydrogen atoms. In the next step, **16→TS16/17→17**, substantial rearrangement occurs with almost no activation. Another hydroboration (HB) step occurs in

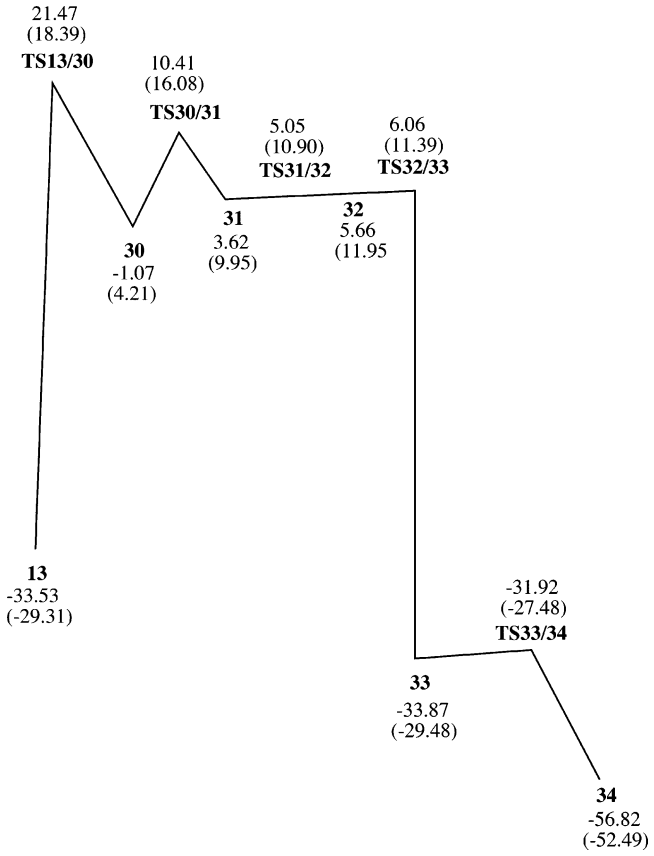

Figure 6. Schematic reaction profile for formation of **34** at the CCSD(T)/6-311+G(d)/MP2/6-31G(d) level. Relative free energies (enthalpies in parentheses) are given in kcal/mol at 298 K relative to allene + B_4H_{10}. All intermediates and transition states contains two H_2 molecules except **13** and **TS13/30** which have one H_2 molecule.

17→TS17/18→18 with $\Delta G^{\ddagger} = 21.3$ kcal/mol to produce an intermediate **18** with an external BH_2 group. In the reaction sequence **18→TS18/19→19→TS19/20→20**, a DSD step takes place in the C_2B_2 unit. In the **20→TS20/21→21** step, a B−C bond is created, while in the **21→TS21/22→22** step, the external BH_2 group is incorporated into the cluster. From **22** to **24**, another DSD step takes place in a CB_3 unit to form an unstable intermediate **24**.[34] The critical C−C bond breaking process **24→TS24/25→25** is compensated by the formation of a C−B bond to form *endo*-2,5-μ-CHMe-1-CB_4H_8 (**25**). There is ambiguity on the orientation of the methyl group in 2,5-μ-CHMe-1-CB_4H_8.[3a,6,12] In ref 6, the methyl group is indicated as *endo* (**25**), while in refs 3a and 12, the product is indicated as *exo* (**26**). The present calculations would suggest that the observed product is **25** rather than **26** because there is a very high free energy barrier of $\Delta G^{\ddagger} = 46.2$ kcal/mol between the two isomers.

The reaction path to form 1-Me-2,5-μ-CH_2-1-CB_4H_7 (**29**) starts at **14** by breaking a C−C bond to form **27** (Figures 3 and 4). From **27** to **28**, a terminal BH_2 group is created which is incorporated into the cluster when **29** is formed. Structure

(33) The brackets are used in the reaction sequence to indicate that the transition state **TS13/14** is lower in energy than the intermediate **14**, which suggests that the actual reaction is **13→TS14/15→15**.

(34) A second pathway from **22→25** was located (not shown) with a BH_2 group pivot which had a free energy lower by 0.6 kcal/mol.

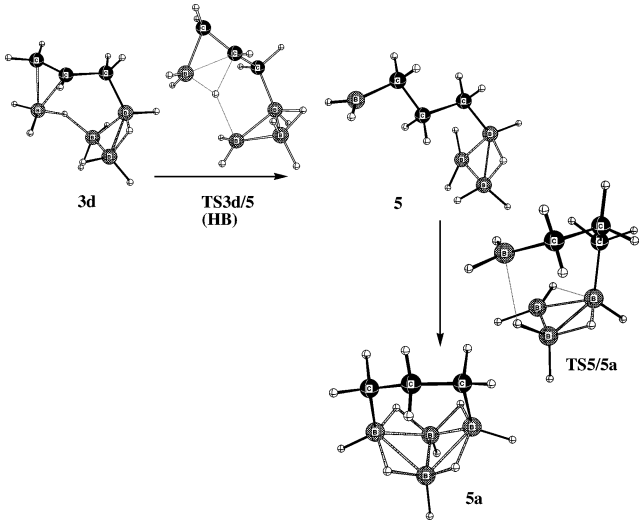

Figure 7. Stationary points for the formation of basket compound **5a**.

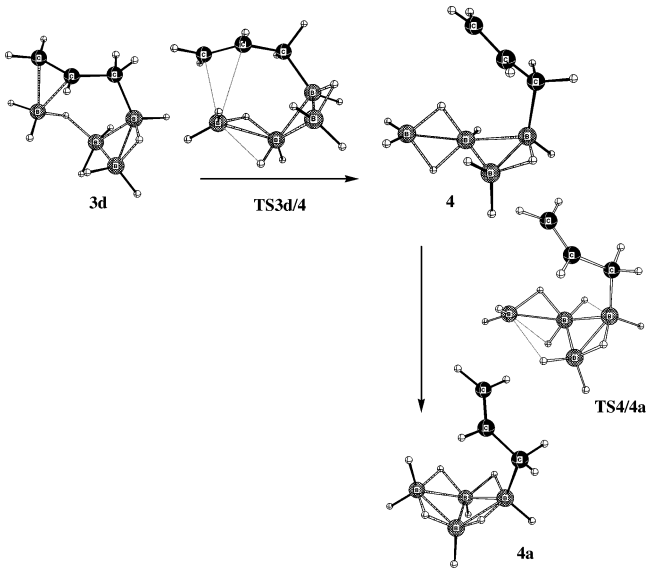

Figure 8. Stationay points for formation of allyl-substituted tetraborane **4a**.

29 is one of the dominant species formed in the reaction between allene and B_4H_{10}.

Starting at structure **13** (Figures 5 and 6) a reaction path was followed for the formation of 2-Me-2,3-$C_2B_4H_7$ (**34**). It would appear that loss of H_2 from **13** would lead to **34**, and indeed it does. However, the H_2-elimination step was computed to have a much higher free energy of activation (**13→TS13/30→30** $\Delta G^{\ddagger} = 55.0$ kcal/mol) than other steps. From the intermediate **30**, four steps with small free energy barriers (**30→31→32→33→34**) lead to the global minimum. Thus, **34** is not formed in the reaction due to the higher barrier for H_2 loss (**13→TS13/30→30**). In the reaction between acetylene and B_4H_8, a $C_2B_4H_{10}$ product is formed which has a relatively low barrier for loss of H_2 to give 2,3-$C_2B_4H_8$ (a demethylated version of **34**) directly. This same reaction pathway would be available for methylacetylene and would lead to 2-Me-2,3-$C_2B_4H_7$ (**34**), but would not be available to allene due to the absence of a C−C triple bond.

An example of intramolecular hydroboration is given by **3d→TS3d/5→5** (Figures 1 and 7) in which the transition

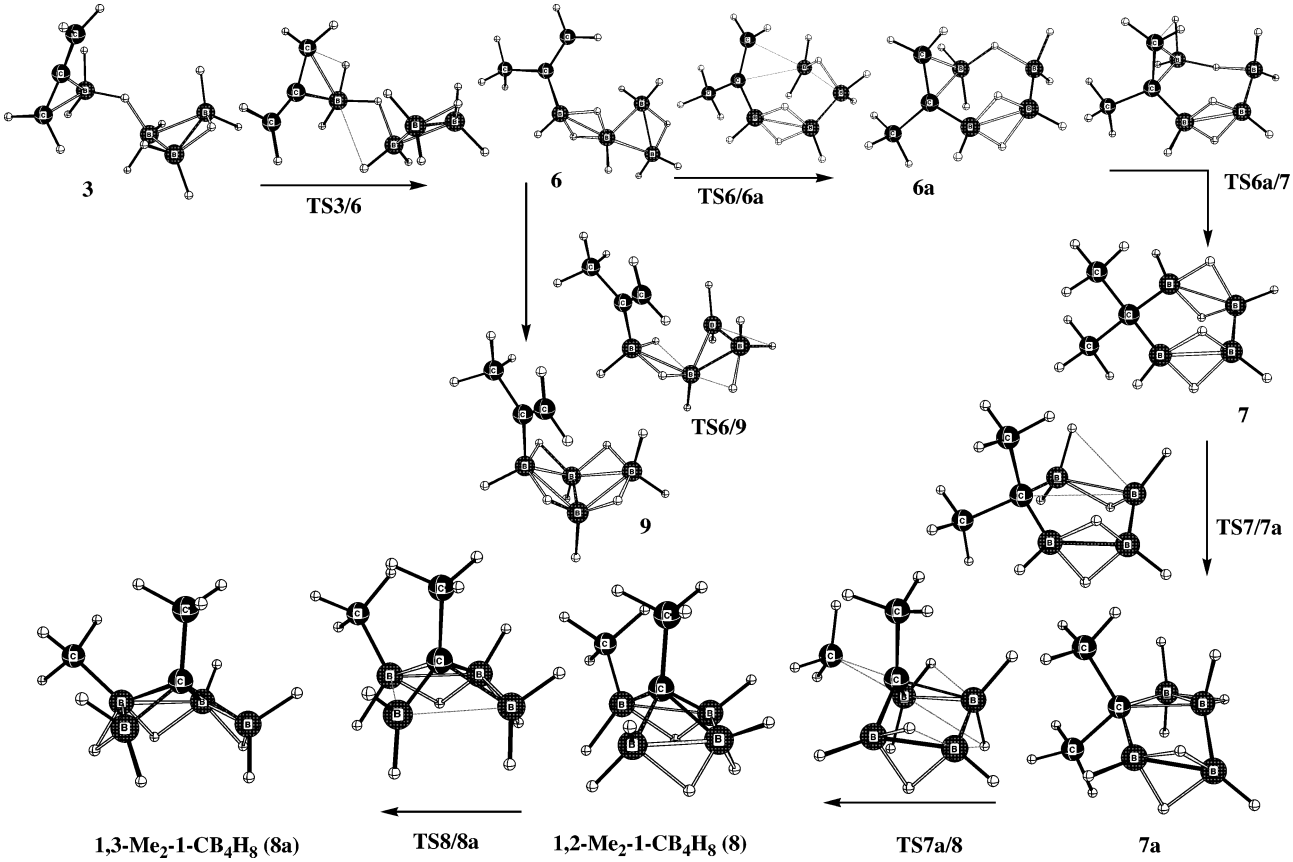

Figure 9. Stationary points along for the formation of *arachno*-1,3- (**8a**) and *arachno*-1-2-Me_2-1-CB_4H_8 (**8**), MP2/6-31G(d) optimized.

state is stabilized by the interaction of the transferring hydrogen with an empty orbital on the B_3H_7-like unit.[18] The product **5**, a derivative of B_3H_7 with a $BH_2-CH_2-CH_2-CH_2$ group, can add the tethered BH_2 to the B_3H_7-like fragment to form **5a**, a 2,4-$(CH_2CH_2CH_2)B_4H_8$ basket, with a free energy of −43.4 kcal/mol. The reaction step (**5→TS5/5a→5a**) is very similar to a related step in the reaction of $B_4H_{10} + C_2H_4$ where the BH_2 end of a tethered $BH_2-CH_2-CH_2$ group adds to the B_3H_7-like unit to form a 2,4-$(CH_2CH_2)B_4H_8$ basket.[18] Both reaction steps are directly analogous to the intermolecular reaction $B_3H_7 + BH_3 \rightarrow B_4H_{10}$ where a terminal hydrogen of the BH_2 group forms a bridging interaction while at the same time the empty p orbital of the BH_2 interacts with a terminal hydrogen in B_3H_7.[16]

Intermediate **3d** can form **4** via the transition state **TS3d/4** where two C−B bonds are broken while a terminal BH bond becomes bridging (Figures 1 and 8). Intermediate **4**, a propenyl-substituted version of **2a**, can form **4a**, a propenyl-substituted tetraborane and a different conformation of **3e**, over a moderate free energy barrier ($\Delta G^{\ddagger} = 23.1$ kcal/mol). The reverse reaction step (**4a→TS4/4a→4**) is analogous to the **2→TS2/2a→2a** reaction where a five-coordinate-boron B_4H_{10} intermedate is formed. In both reactions, a relatively stable species (**4a** and **2**) is converted into a much more reactive intermediate (**4** and **2a**) with free energy barriers of $\Delta G^{\ddagger} = 28.8$ and 26.5 kcal/mol, respectively. The five-coordinate boron is also observed in the structures of **3a** and **6**.

The potential energy surface (Figure 2) shows that there is a competition in formation of basket compounds **1** and **5a**. Even though **1** and **5a** have similar free energies (−43.8 and −43.4 kcal/mol, respectively), **5a** was not observed in the Onak study.[10] This is consistent with the highest transition state free energy in the process **3a→3e→1** (**TS3e/1**, 3.7 kcal/mol) which is 3.6 kcal/mol lower than the highest transition state free energy in the process **3a→3b→3c→3d→5→5a** (**TS3a/3b**, 7.3 kcal/mol).

Monocarbapentaborane isomers *arachno*-1,3- (**8a**) and *arachno*-1,2-Me_2-1-CB_4H_8 (**8**) are synthesized from the quenched reaction of B_4H_{10} with allene in the study by Fox et al.[12] The route from the high-energy intermediate **3** proceeds to **6** with an activation free energy of $\Delta G^{\ddagger} = 5.5$ kcal/mol (**TS3/6**, Figures 9 and 10). From intermediate **6** there are two pathways, one leads to *arachno* isomers **8** and **8a** starting with transition state **TS6/6a** ($\Delta G^{\ddagger} = 20.9$ kcal/mol higher than **6**) and the other forms a propene-substituted borane **9** via transition state **TS6/9** ($\Delta G^{\ddagger} = 18.2$ kcal/mol higher than **6**).

Breaking a B−B bond and forming two C−B bonds in **TS6/6a** leads to **6a** that is 6.2 kcal/mol lower in free energy than B_4H_{10} + allene. The reaction **6a→TS6a/7→7** is a hydroboration step with a modest barrier of $\Delta G^{\ddagger} = 7.0$ kcal/mol to form **7**. The intermediate 2,4-CMe_2-bisdiborane (**7**) has C_{2v} symmetry and is 39.4 kcal/mol lower in free energy than B_4H_{10} + allene. While structure **7** has not yet been reported, it lies in a rather deep free energy well with free

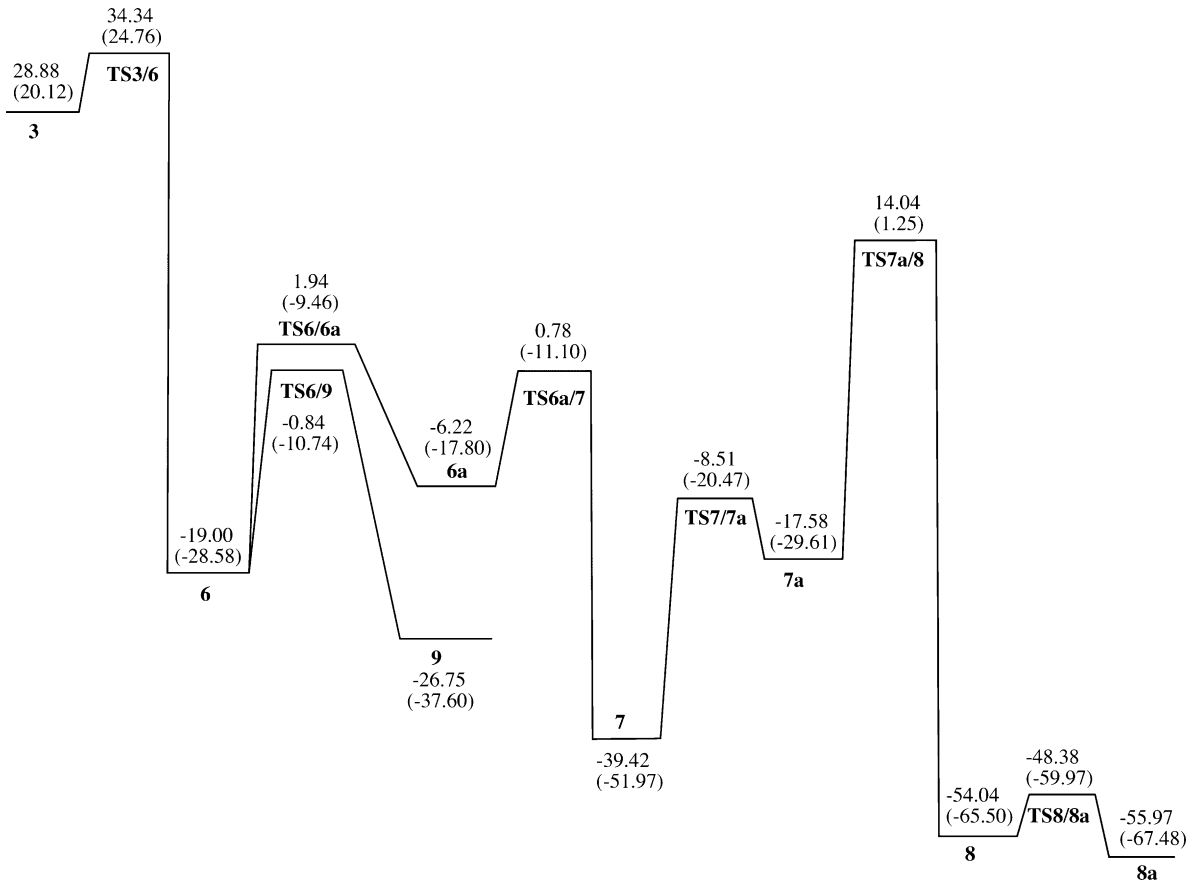

Figure 10. Schematic reaction profile for formation of *arachno*-1,3- (**8a**) and *arachno*-1-2-Me_2-1-CB_4H_8 (**8**) at the CCSD(T)/6-311+G(d)//MP2/6-31G(d) level. Relative free energies (enthalpies in parentheses) are given in kcal/mol at 298 K relative to allene plus B_4H_{10}.

energy barriers of $\Delta G^{\ddagger} = 40.2$ (**7**→**6a**) and 53.5 kcal/mol (**7**→**8**).

The transition state **TS7/7a** was located for the transformation of **7** into **7a** where a BH bridge bond is converted into BH terminal bond. The next step is the migration of a methyl group from carbon to boron (**7a**→**TS7a/8**→**8**) with a free energy barrier of $\Delta G^{\ddagger} = 31.6$ kcal/mol to form *arachno*-1,2-Me_2-1-CB_4H_8 (**8**). Fox et al. assumed that there was a rapid equilibrium between **8** and **8a** with isomer **8a** lower in energy than **8**. Our potential energy surface showed that **8** can easily convert to **8a** through free energy barrier of $\Delta G^{\ddagger} = 5.7$ kcal/mol ($\Delta H^{\ddagger} = 5.5$ kcal/mol). Fox et al.[12] calculated a similar activation barrier for **8**→**TS8/8a**→**8a** ($\Delta H^{\ddagger} = 7.5$ kcal/mol) with a reaction enthalpy of −1.7 kcal/mol which can be compared to our value of $\Delta H_{rxn} = -2.0$ kcal/mol.

Conclusion

The complicated mechanism of carborane formation from boron hydrides plus allene ($B_4H_{10} + C_3H_4$) have been studied computationally. A new basketlike compound **5a** is found which is only slightly less stable than the observed basket **1**. The potential energy surface shows that there is competition for the production of **1** and **5a** and also for the production of *arachno*-1,3- (**8a**) and *arachno*-1,2-Me_2-1-CB_4H_8 (**8**). The production of *arachno*-carbapentaboranes (**25**/**26** and **29**) is less favorable due to a higher free energy of activation barrier for loss of H_2 from B_4H_{10} relative to allene addition.

Acknowledgment. Computer time was made available on the Alabama Supercomputer Network.

Supporting Information Available: MP2/6-31G(d) and CCSD(T)/6-311+G(d) energies (hartrees), zero-point energies (kcal/mol), heat capacity corrections to 298 K (kcal/mol), entropies (cal/mol·K) at the MP2/6-31G(d) level are tabulated in Table S1 and Table S2. Cartesian coordinates of all optimized structures at the MP2/6-31G(d) level are given in Table S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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