Theoretical Study of the Thermochemistry of Molecules in the Si−B−H−Cl System

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A self-consistent set of thermochemical parameters for about 100 molecules in the Si−B−H−Cl system is obtained using a combination of ab initio electronic structure calculations and empirical corrections (the BAC-MP4 method). The species include stable and radical species as well as a few transition states. Trends in calculated heats of formation, bond dissociation enthalpies, and heats of reaction for various molecular decomposition channels are discussed. Silylboranes are most likely to decompose via the elimination of H_2, HCl, or silylenes. The presence of the B atom reduces the energy required for the 1,1 elimination of H_2 from the Si atom, relative to the analogous reaction in disilane.

I. Introduction

Chemical vapor deposition (CVD) is a widely used method for depositing thin films that has important applications in the fabrication of microelectronic devices and protective coatings.[1] In recent years, it has become clear that an improved understanding of the chemistry and physics underlying such a materials-processing method can accelerate the design and optimization of equipment and processes, especially through the use of detailed computational models.[2] Models have been constructed for these chemically reacting flow systems that can include a detailed description of the chemistry,[3] but making the best use of such models requires kinetic parameters for many reactions and thermochemical data for all species considered. Unfortunately, for many cases of interest, such data are not currently available.

One case where an improved chemical understanding, expressed via numerical models, could greatly assist equipment and process design is the CVD of doped materials. The ability to dope materials while depositing them (in situ doping), rather than using separate ion-implantation or dopant in-diffusion steps after deposition, would eliminate a number of processing steps. The addition of small amounts of dopant-source gases to CVD processes, however, is often accompanied by sufficiently large changes in deposition rate and detrimental effects on deposition uniformity that such processes are generally not used. For p-type dopants, the use of diborane generally leads to increases in the deposition rate. For deposition of silicon from silane, the addition of a small amount of diborane (1.5×10^{-3} of the silane concentration) is reported to double the deposition rate.[4] For disilane, the addition of diborane (2×10^{-4} of the disilane concentration) is reported to increase the deposition rate by more than a factor of 3 at lower temperatures,[5,6] although the effect decreases with increasing temperature.[5,7] For dichlorosilane, the addition of diborane (1×10^{-3} of the dichlorosilane concentration) is reported to increase the deposition rate by 2 orders of magnitude.[8] In contrast, for n-type dopants, the use of phosphine and arsine are reported to decrease deposition rates with silane,[4] while increasing deposition rates with dichlorosilane.[8]

It is generally believed that these dopant-source gases are altering the rates of reactions occurring at the silicon surface. Even after a great deal of work,[9,10] however, the details of hydrogen bonding and reactions on silicon surfaces in the absence of dopants are not fully understood, much less in the presence of dopants. In such situations, we have found that an understanding of analogous gas-phase reactions can be useful guides for evaluating proposed surface reactions, especially when they involve covalent rather than metallic bonding. In addition, it is possible, though unlikely under the process conditions used in many production CVD systems, that gas-phase reactions occur forming silylboranes, which then alter deposition rates in the CVD of boron-doped silicon.

In this paper, we present calculations on molecules in the Si−B−H−Cl system, which provide useful insights into bonding geometries and energies, and heats of reaction. Studies of the smaller molecular systems allow us to explore a wide variety of bonding configurations while obtaining sufficiently accurate information on geometries and energetics. We use a combination of ab initio electronic structure calculations and empirical bond additivity corrections (BACs) to obtain thermochemical data for about 100 molecules, specifically the $SiBH_n$ ($n \leq 5$), Si_2BH_n ($n \leq 7$), SiB_2H_n ($n \leq 6$), and $SiBH_nCl$ ($n \leq 4$) species. We include both stable and radical species, as well as a few transition states for key decomposition reactions. We have previously applied these methods to a number of chemical systems important for modeling CVD and combustion, including numerous compounds composed of first-row elements,[11] the Si−H,[12,13] Si−H−Cl,[12] Si−N−H−F,[14,15] Si−C−Cl−H,[16,17] Si−O−H−C,[18,19] and B−N−Cl−H[20] systems. The thermochemical data for the Si−B−H−Cl species presented here form a self-consistent set with the data from these previous works.

A number of the Si−B−H species have been the subject of previous quantum chemistry studies. Mains, Trachtman, and Bock published a series of papers on silylboranes,[21,22] fluorine substituted silylboranes,[23−25] unsaturated silicon boron hydrides,[26] and a few transition states for H_2 elimination.[27] Luke et al.[28,29] included the $SiBH_x$ ($x = 1, 3, 5$) species in their studies of substituted silicon and carbon compounds. Schleyer and

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Kost[30] included a few Si−B−H species in their study of π-bond energies of C and Si compounds, as did Coolidge and Borden[31] in their study of substituent effects on silyl and methyl radical stabilization. Subramanian and co-workers studied the isomers of SiB_2H_4[32] and Si_2BH_3.[33]

Some of the Si−B−H−Cl species, particularly the less saturated ones, are of interest because of their unusual structures and chemical bonding. A number of these species have H atoms bridge-bonded between the Si and the B and/or cyclic structures. In this paper, the nomenclature Si(H)B denotes a H bridge bonded between a Si and a B, whereas −HSiBHSiH− denotes a cyclic species with one H atom bonded to each of the silicons and the boron. Such structures will be discussed in more detail in section III.A. In the tables, transition states are indicated by writing out a reaction; i.e., $H_3SiBH_2 \rightarrow SiH_2 + BH_3$ represents the transition state for silylene elimination from silylborane.

II. Theoretical Methods

The theoretical methods used in this work have been described elsewhere,[11,14] so we present only a short description here. Our choice of theoretical method represents a compromise between using sufficiently high levels of theory to get accurate results and the ability to handle molecules with a reasonably large number of heavy atoms.

Electronic structure calculations are done using Gaussian 94[34] and earlier versions of these quantum chemistry codes. Equilibrium geometries and harmonic vibrational frequencies are obtained at the HF/6-31G* level of theory (restricted Hartree−Fock theory, RHF,[35] for the closed-shell molecules and unrestricted Hartree−Fock theory, UHF,[36] for the open-shell molecules, using the 6-31G* basis set[37,38]). This level of theory provides sufficiently accurate equilibrium geometries but does not provide total energies suitable for determining reaction energies involving the breaking of covalent bonds. Vibrational frequencies calculated at this level of theory are known to be systematically larger than experimental values[39] so each calculated frequency has been scaled by dividing it by 1.12.

To determine atomization enthalpies, and thus heats of formation, the effects of electron correlation are included by performing single-point calculations, using Moller−Plesset perturbation theory, at the HF/6-31G* geometries. In most cases, MP4(SDTQ)/6-31G** calculations (fourth-order perturbation theory with single, double, triple, and quadruple substitutions using the 6-31G** basis set) are done. This level of theory has been used in most of the previous work; the errors remaining in the total energies are sufficiently systematic that the bond additivity corrections provide enthalpies good to a few kcal mol^{-1}. However, we believe that transition-state energies calculated with this method tend to be systematically high by several kcal mol^{-1}.

Empirical BACs are used to account for systematic errors in the ab initio calculations, which result primarily from basis set truncation. The BACs depend mainly on the bond type and bond length, but there are also corrections based on the types of the neighboring atoms. For the example of the chemical bond between atoms X_i and X_j in the molecule $X_k-X_i-X_j$, the BAC has the form $BAC(X_i-X_j) = f_{ij}g_{kij}$, where $f_{ij} = A_{ij}\exp(-\alpha_{ij}R_{ij})$, $g_{kij} = (1 - h_{ik}h_{ij})$, and $h_{ik} = B_k\exp[-\alpha_{ik}(R_{ik} - 1.4\ \text{Å})]$. A_{ij} and α_{ij} are empirical parameters that depend on the bond type X_i-X_j, and R_{ij} is the bond distance (in angstroms) from the HF geometry. The parameter B_k, used in the neighboring-atom correction factor g_{kij}, depends on the type of atom k. In the case of a chemical bond between atoms X_i and X_j in the molecule $X_k-X_i-X_j-X_l$, the added heavy atom leads to a similar neighboring-atom correction factor, and the BAC has the form $BAC(X_i-X_j) = f_{ij}g_{kij}g_{lji}$.

TABLE 1: Parameters[a] Used in Bond Additivity Corrections

bond	A	α
H−H	18.98	2.0
B−H	31.12	2.0
B−Cl	172.49	2.0
B−B	969.8	3.8
Si−H	92.79	2.0
Si−B	45.77	1.0
Si−Cl	721.93	2.0
Si−Si	3330.21	2.7
H−Cl	116.40	2.0
atom	B	energy (hartrees)
H	0.0	−0.498 232 0
B	0.2	−24.576 225 8
Si	0.2	−288.887 943 0
Cl	0.42	−459.570 273 7

[a] See text for parameter definitions.

Table 1 lists the values for A_{ij}, α_{ij}, and B_k used in this (and previous) work. For Si−H, Si−Si, and Si−Cl bonds, silane, disilane, and tetrachlorosilane are used as reference compounds to determine A_{ij} values, while α values are determined by analogy with related classes of compounds. For B−Cl bonds, BCl_3 was the reference compound. As discussed elsewhere,[20] the BACs for B−H were determined using a G2 calculation[40] as a reference because of large uncertainties in the recommended heats of formation in the literature for BH_n compounds. Corrections for B−B bonds were needed for a few of the $Si_1B_2H_n$ compounds. A_{BB} was determined by using G2 calculations for B_2H_4 (see the Supporting Information for results from the G2 calculations), while α_{BB} was set to the value determined for C−C bonds.[11] There is little thermochemical data in the literature for species in the Si−B−H−Cl system, so we determined the BAC parameters for Si−B using G2 calculations of the atomization energies for H_3SiBH_2 and $H_2Si{=}BH$. Values for B_H, B_{Cl}, and B_{Si} were determined previously.[11,14] The B_B value was chosen to be consistent with the other first-row elements.

There is an additional BAC for spin. For open-shell molecules, the unrestricted Hartree−Fock (UHF) method leads to spin contamination errors that are approximated using the Moller−Plesset projection approximations of Schlegel.[41] The BAC(spin S^2) is defined as the difference between the energy calculated with the MP3 level of theory using the UHF wave function (E(UMP3)) and the projected UMP3 energy (E(PUMP3)).[40] For closed-shell molecules that are UHF unstable (e.g., SiH_2), we use a correction, BAC(spin UHF-I), defined as $K_{UHF-I}S(S + 1)$, where S is the spin obtained from the UHF/6-31G** calculation and K_{UHF-I} has the value of 10.0 kcal mol^{-1}, based on O_3.

Table 2 lists calculated bond lengths for each species in this study, as well as the BACs corresponding to each bond and any spin corrections. The BACs listed are those for the highest level of theory, MP4(SDTQ). The sum of these bond additivity corrections are combined with the electronic energy and the unscaled zero-point energy to obtain the heat of formation (ΔH°_f) at 0 K. From the heats of formation at 0 K, statistical-mechanics equations involving the calculated geometries and scaled frequencies give entropies, heat capacities, enthalpies, and free energies at other temperatures. For historical reasons, the unscaled frequencies are used for determining $\Delta H^\circ_f(0)$ while the scaled frequencies are used to calculated thermochemistry at higher temperatures. Minor differences that would result from using the scaled frequencies to calculate $\Delta H^\circ_f(0)$ are incorporated into the BACs.

TABLE 2: Calculated Bond Lengths (Å) with Degeneracies[a] and Corresponding Bond Additivity Corrections (kcal mol^{-1}) for the MP4(SDTQ) Level of Theory

species	Si−B bond length	BAC	Si−H bond length	BAC	B−H bond length	BAC	other[b]	bond length	BAC
H_3SiBH_2	2.040	5.95	1.483	4.78	1.190(2)[a]	2.88			
			1.479(2)	4.81					
$HSi(H_2)BH_2$	2.188	5.13	1.656(2)	3.28	1.186	2.90			
			1.499	4.63	1.188	2.89			
					1.314(2)	2.18			
H_2SiBH_2	1.954	6.48	1.471(2)	4.89	1.188(2)	2.89	spin		0.43
$Si(H_2)BH_2$	2.198	5.08	1.667(2)	3.22	1.189(2)	2.89	spin		0.74
					1.310(2)	2.20			
$HSi(H)BH_2$	1.971	6.37	1.490	4.71	1.184	2.92	spin		1.15
			1.707	2.98	1.189	2.89			
					1.341	2.08			
H_3SiBH	2.015	6.10	1.479(2)	4.82	1.184	2.91	spin		0.29
			1.481	4.80					
$HSi(H_2)BH$	2.164	5.26	1.501	4.62	1.294(2)	2.27	spin		0.33
			1.677(2)	3.15	1.183	2.92			
$Si(H_2)BH$	1.811	7.48	1.732(2)	2.83	1.177	2.96			
					1.314(2)	2.19			
$Si(H)BH_2$	1.912	6.77	1.610	3.63	1.530	1.43	UHF		1.31
					1.195(2)	2.85			
$HSiBH_2$ $^1A'$	2.013	6.11	1.514	4.49	1.194(2)	2.86	UHF		3.14
H_2SiBH $^1A_1$	1.819	7.42	1.466(2)	4.94	1.171	2.99	UHF		2.61
$HSiBH_2$ $^3A''$	1.976	6.34	1.479	4.82	1.189	2.89	spin		0.21
					1.187	2.90			
H_2SiBH $^3A''$	1.913	6.76	1.470	4.90	1.182	2.93	spin		0.41
			1.474	4.86					
H_3SiB	2.136	5.40	1.481(3)	4.80			UHF		6.44
$Si(H_3)B$	2.007	6.15	1.608(3)	3.63	1.400(3)	1.84			
$SiBH_2$	1.980	6.32			1.194(2)	2.86	spin		0.31
$HSiBH$	1.907	6.80	1.514	4.49	1.178	2.95	spin		0.54
$Si(H_2)B$	1.831	7.34	1.825(2)	2.36	1.276(2)	2.37	spin		3.32
H_2SiB	1.934	6.62	1.480(2)	4.81			spin		0.74
$SiBH$ $^3\Sigma^-$	1.859	7.13			1.178	2.95	spin		0.50
$SiBH$ $^1\Delta$	1.881	6.97			1.177	2.96	UHF		10.06
$HSiB$ $^3A''$	1.935	6.61	1.516	4.47			spin		0.28
SiB	1.847	7.22					spin		13.40
$H_3SiBH_2 \rightarrow SiH_2 + BH_3$	2.140	5.39	1.515	4.37	1.184(2)	2.91	UHF		4.29
			1.468(2)	4.92	1.493	1.53			
$H_3SiBH_2 \rightarrow HSiBH_2 + H_2$	1.979	6.32	1.627	3.58	1.189(2)	2.89	H−H	1.020	2.47
			1.556	4.13					
			1.478	4.82					
$HSiBH_2 \rightarrow Si(H)BH_2$	1.928	6.65	1.582	3.86	1.696	1.03	UHF		1.24
					1.194(2)	2.86			
$Si(H)BH_2 \rightarrow Si(H_2)BH$	1.861	7.12	1.644	3.38	1.414	1.80			
			2.241	1.04	1.182	2.93			
					1.227	2.65			
$H_3SiSiH_2BH_2$	2.035	5.97	1.482(2)	4.79	1.190(2)	2.88	Si−Si	2.364	5.63
			1.478	4.83					
			1.479(2)	4.82					
$HB(SiH_3)_2$	2.040(2)	5.88	1.479(4)	4.82	1.192	2.87			
			1.483(2)	4.78					
$H_2SiBHSiH_3$	2.034	5.91	1.481(2)	4.80	1.191	2.88	spin		0.41
	1.945	6.47	1.480	4.81					
			1.471(2)	4.89					
$H_3SiBSiH_3$	2.008(2)	6.07	1.478(2)	4.83			spin		0.42
			1.480(2)	4.81					
			1.481(2)	4.80					
$Si(H_2)BSiH_3$	1.818	7.33	1.751(2)	2.73	1.302(2)	2.25			
	2.011	6.04	1.479(3)	4.82					
$-H_2SiBHSiH_2-$ (cyc)	1.894(2)	6.78	1.470(2)	4.90	1.184	2.91	Si−Si	2.639	2.68
			1.474(2)	4.87					
$Si(H)BHSiH_3$	1.880	6.90	1.651	3.33	1.414	1.80	UHF		0.47
	2.049	5.82	1.479(2)	4.81	1.191	2.88			
			1.485	4.76					
$H_3SiSiBH_2$	1.986	6.27	1.478	4.83	1.194(2)	2.86	UHF		3.02
			1.480	4.81			Si−Si	2.404	5.04
			1.481	4.80					
$HSiBHSiH_3$	1.999	6.13	1.514	4.49	1.195	2.85	UHF		2.67
	2.046	5.85	1.480(3)	4.81					
$H_3SiSiHBH$	1.824	7.37	1.472	4.89	1.172	2.98	UHF		2.86
			1.477	4.84			Si−Si	2.331	6.14
			1.476(2)	4.85					
$H_2SiBSiH_3$	1.828	7.26	1.468(2)	4.92			UHF		3.09
	2.002	6.09	1.477(2)	4.84					
			1.479	4.81					

TABLE 2 (Continued)

species	Si−B bond length	BAC	Si−H bond length	BAC	B−H bond length	BAC	other^b	bond length	BAC
$Si(H_2)BSiH_2$	1.826	7.27	1.744(2)	2.76	1.301(2)	2.25	spin		0.89
	1.996	6.13	1.478(2)	4.83					
$-H_2SiBHSiH-$ (cyc)	2.060	5.76	1.475	4.86	1.181	2.93	Si−Si	2.278	7.08
	1.974	6.27	1.478	4.83					
			1.476	4.84					
$-H_2SiBSiH_2-$ (cyc)	1.881(2)	6.86	1.474(2)	4.87			Si−Si	2.622	2.80
			1.476(2)	4.85					
$HSiBHSiH_2$	2.015	6.03	1.505	4.58	1.193	2.86	spin		3.88
	1.975	6.27	1.474	4.87					
			1.475	4.86					
$Si(H_2)BHSiH$	2.063	5.76	1.505	4.57	1.194	2.86	spin		4.62
	2.189	5.08	1.667	3.21	1.306(2)	2.22			
			1.669	3.20					
HSi(H)BHSiH	1.983	6.22	1.492	4.69	1.341	2.07	spin		5.22
	2.028	5.95	1.502	4.60	1.193	2.86			
			1.697	3.04					
$-Si(H)SiBH_2-$ (cyc)	1.993(2)	6.15	1.624(2)	3.55	1.190(2)	2.88	Si−Si	2.341	5.97
−HSiBHSiH− (cyc)	1.931	6.52	1.474(2)	4.87	1.181	2.93	Si−Si	2.106	11.22
	1.930	6.53							
−Si(H)BH(H)Si− (cyc)	2.067(2)	5.72	1.706(2)	2.98	1.284(2)	2.32	Si−Si	2.292	6.82
					1.184	2.92			
−HSiSi(H)BH− (cyc)	2.410	4.07	1.463	4.98	1.183	2.92	Si−Si	2.174	9.36
	1.894	6.80	1.830	2.33	1.249	2.50			
$-SiBHSiH_2-$ (cyc)	1.909	6.68	1.472	4.89	1.184	2.92	UHF		4.21
	1.867	6.96	1.476	4.85			Si−Si	2.699	2.28
$H_2BSi(H)Si$	1.992	6.23	1.853	2.26	1.188	2.89	UHF		1.71
			1.604	3.71	1.190	2.88	Si−Si	2.196	8.84
$Si(H_2)BSiH$	1.825	7.28	1.744	2.76	1.298	2.27	UHF		3.55
	2.019	5.99	1.722	2.89	1.309	2.21			
			1.511	4.52					
Si(H)BHSiH	2.034	5.91	1.512	4.51	1.204	2.80	UHF		5.11
	1.893	6.80	1.612	3.61	1.501	1.51			
$HSiBSiH_2$	1.845	7.13	1.468(2)	4.93			UHF		4.87
	1.934	6.52	1.513	4.50					
HSiBHSiH	2.007(2)	6.08	1.513(2)	4.50	1.203	2.81	UHF		6.09
$H_2Si(BH_2)_2$	2.044(2)	5.86	1.483(2)	4.78	1.190(4)	2.88			
$HSi(BH_2)_2$	1.993(2)	6.16	1.477	4.84	1.189(4)	2.89	spin		0.41
$HBSiH_2BH_2$	2.044	5.86	1.486	4.75	1.189	2.88	spin		0.34
	2.018	6.02	1.481	4.79	1.191	2.88			
					1.185	2.91			
−BH(H)Si(H)BH− (cyc)	1.946(2)	6.39	1.836(2)	2.30	1.178(2)	2.95	B−B	1.663	1.72
					1.212(2)	2.69			
−HBBH(H)SiH− (cyc)	2.003	6.03	1.635	3.42	1.296	2.26	B−B	1.634	1.91
	1.821	7.22	1.469	4.91	1.183	2.92			
					1.175	2.97			
−HB(H)BHSiH− (cyc)	1.859(2)	6.99	1.464	4.96	1.322(2)	2.09	B−B	1.823	0.94
					1.182(2)	2.93			
$-H_2SiBHBH-$ (cyc)	2.322	4.40	1.473(2)	4.87	1.173	2.98	UHF		1.89
	1.902	6.66			1.179	2.94	B−B	1.526	2.87
$Si(BH_2)_2$	1.985(2)	6.21			1.192(4)	2.87	UHF		0.32
H_2BBSiH_2	1.834	7.24	1.468(2)	4.93	1.192(2)	2.87	UHF		4.29
							B−B	1.630	1.96
$H_2BBHSiH$	2.013	6.07	1.513	4.50	1.194(2)	2.86	UHF		2.90
							B−B	1.671	1.68
$H_3SiBHCl$	2.042	5.81	1.475	4.85	1.185	2.91	B−Cl	1.762	4.98
			1.479(2)	4.82					
$H_2ClSiBH_2$	2.032	5.93	1.474(2)	4.87	1.190	2.88	Si−Cl	2.081	11.11
					1.187	2.90			
$ClSi(H_2)BH_2$	2.188	5.08	1.669(2)	3.20	1.304(2)	2.23	Si−Cl	2.100	10.73
					1.185	2.91			
					1.189	2.89			
$HSi(H_2)BHCl$	2.198	4.99	1.494	4.67	1.314(2)	2.18	B−Cl	1.794	4.68
			1.661(2)	3.25	1.183	2.92			
$HSi(HCl)BH_2$	2.478	3.79	1.496	4.66	1.181(2)	2.93	B−Cl	1.975	3.28
			1.671	3.19	1.315	2.18	Si−Cl	2.293	7.30
$HClSiBH_2$	1.983	6.23	1.470	4.90	1.188	2.89	Si−Cl	2.072	11.32
					1.186	2.91	spin		0.74
$H_2SiBHCl$	1.994	6.09	1.474	4.87	1.184	2.92	B−Cl	1.765	4.94
			1.472	4.88			spin		0.58
$ClSi(H)BH_2$	2.039	5.89	1.814	2.41	1.185	2.91	Si−Cl	2.081	11.13
					1.186	2.90	spin		1.98
					1.281	2.35			
$Si(H_2)BHCl$	2.212	4.93	1.673(2)	3.17	1.183	2.92	B−Cl	1.800	4.64
					1.309(2)	2.21	spin		0.77

TABLE 2 (Continued)

species	Si−B bond length	BAC	Si−H bond length	BAC	B−H bond length	BAC	other[b]	bond length	BAC
H_3SiBCl	2.028	5.89	1.478	4.83			B−Cl	1.736	5.23
			1.477(2)	4.84			spin		0.31
HSi(H)BHCl	2.030	5.88	1.493	4.68	1.184	2.92	B−Cl	1.781	4.80
			1.752	2.72	1.300	2.25	spin		1.84
$H_2ClSiBH$	2.000	6.12	1.471(2)	4.89	1.181	2.93	Si−Cl	2.085	11.03
							spin		0.31
$ClSi(H_2)BH$	2.163	5.21	1.703(2)	2.99	1.276(2)	2.36	spin		0.38
					1.182	2.93	Si−Cl	2.100	10.73
$Si(H_2)BCl$	1.813	7.27	1.730(2)	2.85	1.320(2)	2.17	B−Cl	1.751	5.05
$ClSiBH_2$	2.044	5.87			1.192(2)	2.87	UHF		2.62
							Si−Cl	2.120	10.30
HSiBHCl	2.038	5.84	1.511	4.52	1.188	2.89	UHF		3.48
							B−Cl	1.774	4.86
H_2SiBCl	1.859	6.92	1.472(2)	4.89			UHF		4.88
							B−Cl	1.690	5.70
HClSiBH	1.811	7.37	1.459	5.01	1.170	3.00	UHF		5.50
							Si−Cl	2.056	11.65
$ClSi(H_2)B$	2.315	4.48	1.673(2)	3.18	1.355(2)	2.02	UHF		5.69
							Si−Cl	2.106	10.61
$SiBCl_2$	2.021	5.81					B−Cl	1.769(2)	4.71
							spin		0.37
ClSiBCl	1.971	6.14					Si−Cl	2.120	10.29
							B−Cl	1.701	5.60
							spin		2.85
SiBHCl	2.009	6.01			1.188	2.89	B−Cl	1.779	4.81
							spin		0.35
HSiBCl	1.913	6.57	1.513	4.50			B−Cl	1.695	5.66
							spin		0.55
ClSiBH	1.960	6.38			1.178	2.95	Si−Cl	2.125	10.18
							spin		2.57
HClSiB	1.976	6.27	1.478	4.83			Si−Cl	2.085	11.03
							spin		1.36
SiBCl $^3\Sigma$	1.869	6.86					B−Cl	1.701	5.58
							spin		0.59
SiBCl $^1\Sigma$	1.886	6.74					B−Cl	1.697	5.63
							UHF		10.07
ClSiB $^1A'$	1.936	6.52					Si−Cl	2.091	10.89
							UHF		12.84
ClSiB $^3\Sigma^-$	1.764	7.71					Si−Cl	2.020	12.49
							spin		3.10
HClSi:BH3			1.504	4.58	1.189(3)	2.89	UHF		2.14
							Si−Cl	2.100	10.82
$H_2Si:BH_2Cl$			1.509(2)	4.53	1.178	2.95	UHF		1.88
					1.179	2.94	B−Cl	1.765	5.06
$H_3SiBHCl \rightarrow SiH_2 + BH_2Cl$	2.156	5.20	1.467	4.93	1.181	2.94	UHF		3.46
			1.470	4.90	1.518	1.46	B−Cl	1.759	5.02
			1.516	4.37					
$H_2ClSiBH_2 \rightarrow SiH_2 + BH_2Cl$	2.240	4.78	1.458(2)	5.02	1.179(2)	2.94	UHF		5.78
							B−Cl	1.984	3.22
							Si−Cl	2.162	9.45
$HSi(HCl)BH_2 \rightarrow SiHCl + BH_3$	2.848	2.64	1.499	4.62	1.180(2)	2.94	B−Cl	2.612	0.93
					1.220	2.71	Si−Cl	2.155	9.64
$H_2ClSiBH_2 \rightarrow ClSi(H_2)BH_2$	2.119	5.44	1.475	4.82	1.186(2)	2.91	UHF		2.47
			1.485	4.69	1.802	0.83	Si−Cl	2.079	11.18
					2.072	0.49			
$H_2ClSiBH_2 \rightarrow HSiBH_2 + HCl$	2.015	6.08	1.695	3.02	1.186	2.91	UHF		3.06
			1.482	4.79	1.190	2.88	Si−Cl	2.670	3.45
							H−Cl	1.531	5.25
$[HClSi(H)BH_2] \rightarrow HSiBH_2 + HCl$	2.056	5.83	1.490	4.71	1.186	2.90	Si−Cl	2.488	4.96
					1.192	2.87	H−Cl	1.502	5.56
					1.703	0.99			

[a] A number in parentheses after a bond length indicates the number of bonds of that type and length in the molecule. [b] "UHF" indicates a correction for UHF instability; "spin" indicates a correction for spin contamination.

There are two primary sources of uncertainty in the calculated heats of formation: uncertainties resulting from the applicability of the theoretical methods to a given molecule and systematic uncertainties resulting from lack of good reference compounds for the BACs.

For the uncertainty in the theoretical methods, we have an ad hoc technique for estimating the error in the BAC-MP4 heats of formation that uses the results from lower-level calculations. The error estimate is given by error(BAC-MP4) = $[1.0\ \text{kcal mol}^{-1} + (\Delta H_{\text{BAC-MP4}} - \Delta H_{\text{BAC-MP3}})^2 + (\Delta H_{\text{BAC-MP4}} - \Delta H_{\text{BAC-MP4(SDQ)}})^2 + 0.25\ (\text{BAC(spin } S^2) \text{ or BAC(spin UHF-I)})^2]^{1/2}$, where we use the notation BAC-MP4 to refer specifically to the BAC-MP4(SDTQ) results, and an inherent uncertainty of 1.0 kcal mol^{-1} has been included. This formula provides a measure of the consistency of the results across levels of theory, which in turn is related to the confidence we have in

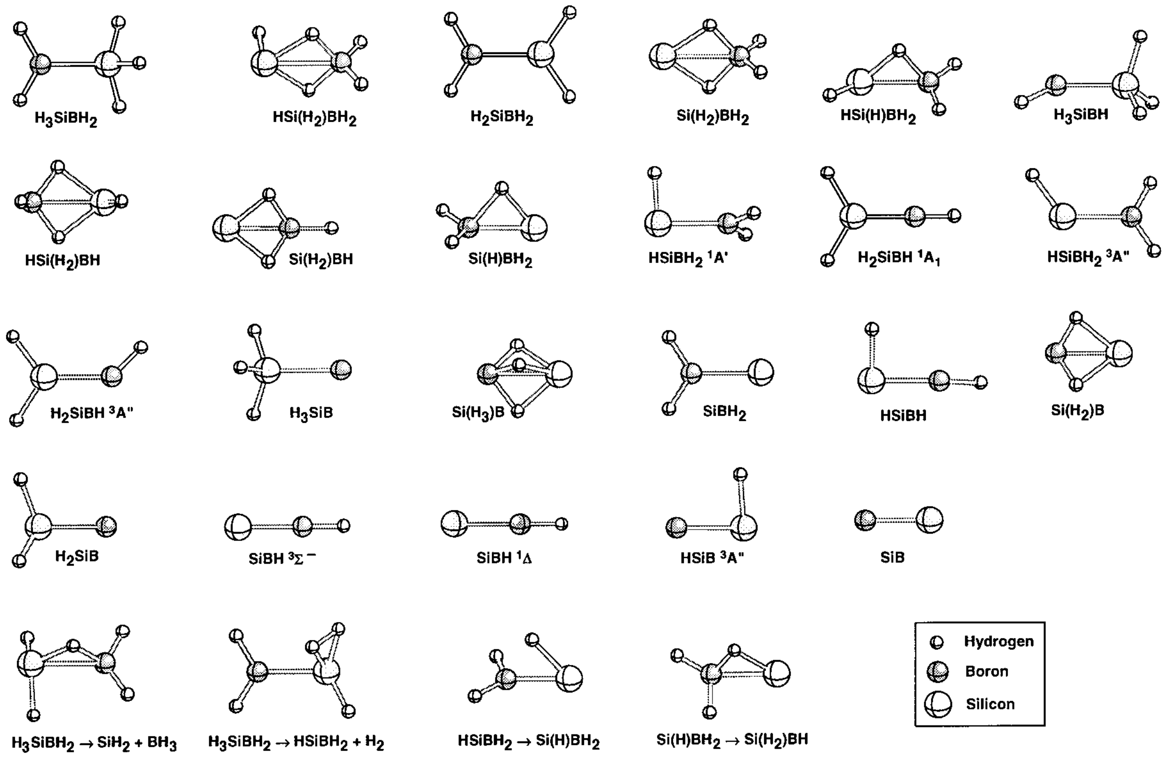

Figure 1. HF/6-31G* structures for $SiBH_n$ compounds.

the BAC-MP4 results. However, some species, such as HSiBCl and ClSiBCl, do not have same minima at the Hartree−Fock and higher levels of theory. To maintain uniformity, we always used the HF minimum as the geometry for the single-point, perturbation theory energy calculations in this work. But this does represent an additional source of uncertainty that could add a few kcal mol^{-1} to the estimates derived using the above formula.

The second major source of uncertainty, lack of good reference compounds, can add a few more kcal mol^{-1} to the uncertainty estimates and will scale with the number of bonds in the molecule. The use of different reference values would tend to shift our calculated heats of formation as a group, so calculated bond dissociation enthalpies and reaction enthalpies would be altered less than the heats of formation. Overall, we believe that the uncertainties in these BAC-MP4 heats of formation lie in the range 3−8 kcal mol^{-1}, with the larger values corresponding to the larger or more unsaturated systems, particularly those that involve unusual bonding.

III. Results and Discussion

In this paper, we cover a variety of Si−B−H−Cl species, but this is not a comprehensive study of all possible permutations of these elements. We treat the $SiBH_n$ ($n \leq 5$) species in the most detail; we include results for a number of higher-energy isomers and electronically excited states, as well as transition states for four decomposition reactions. We treat the Si_2BH_n ($n \leq 7$) and SiB_2H_n ($n \leq 6$) species in less detail; we include fewer high-energy isomers, fewer highly unsaturated species, and no transition states. For chlorinated compounds, we cover most of the $SiBH_nCl$ ($n \leq 4$) species; we include a variety of higher-energy isomers, several adducts and transition states, plus $SiBCl_2$ and ClSiBCl.

The focus of this paper is thermochemistry rather than the electronic structure calculations per se. Therefore, this section primarily presents and discusses the thermochemical results, while the Supporting Information, described in the Appendix, provides the detailed results of the electronic structure calculations. A number of species, however, exhibit sufficiently unusual structures that we include a section discussing molecular geometries, although the numerical details of these structures are given only in the Supporting Information.

A. Bonding in Si−B−H−Cl Molecules. The HF/6-31G* geometries found for the molecules studied in this paper are shown in Figures 1−3. There are a number of interesting features, particularly among the less saturated species. The most notable of these are the presence of the bridge-bonded H atoms and the prevalence of cyclic isomers in the larger molecules. Rather than discussing every molecule in detail, we use a few examples to illustrate interesting points. A number of features of the bonding in the $SiBH_n$ ($n = 1-5$) species have been discussed by Mains and co-workers,[25] so we do not repeat such material here.

The H atoms bridge-bonded to both Si and B in these Si−B−H−Cl compounds are analogous to bridged H bonds observed in other compounds. The bond lengths are somewhat longer than normal: 1.6−1.7 Å rather than 1.5 Å for Si−H bonds and 1.3−1.5 Å rather than 1.2 Å for B−H bonds. Bridged bonds are well-known in compounds such as the boron hydrides and Al_2Cl_6.[42] In computational studies, bridged H bonds were predicted for unsaturated Si_2H_n species, with $Si(H_2)Si$ drawing the most attention.[43] Such structures were subsequently confirmed by spectroscopic experiments.[44]

In a number of cases, we found that plausible bridged structures, especially singly bridged species, were not stable at our level of theory. For example, $H_2Si(H)BH_2$ was not stable at the HF/6-31G* level of theory we used for the geometry optimizations, but rather opened up to normal H_3SiBH_2 geometry. Similarly, Si(H)BHCl opened to HSiBHCl, Si(H)BH opened to $SiBH_2$, and ClSi(H)BH opened to $ClSiBH_2$. In contrast, attempts to find a stable HSi(H)BH were not successful because the H on the Si preferred to move into a bridged position, resulting in the $Si(H_2)BH$ species. Although Si(H)Si is the most stable form of Si_2H,[45] we did not find an analogous

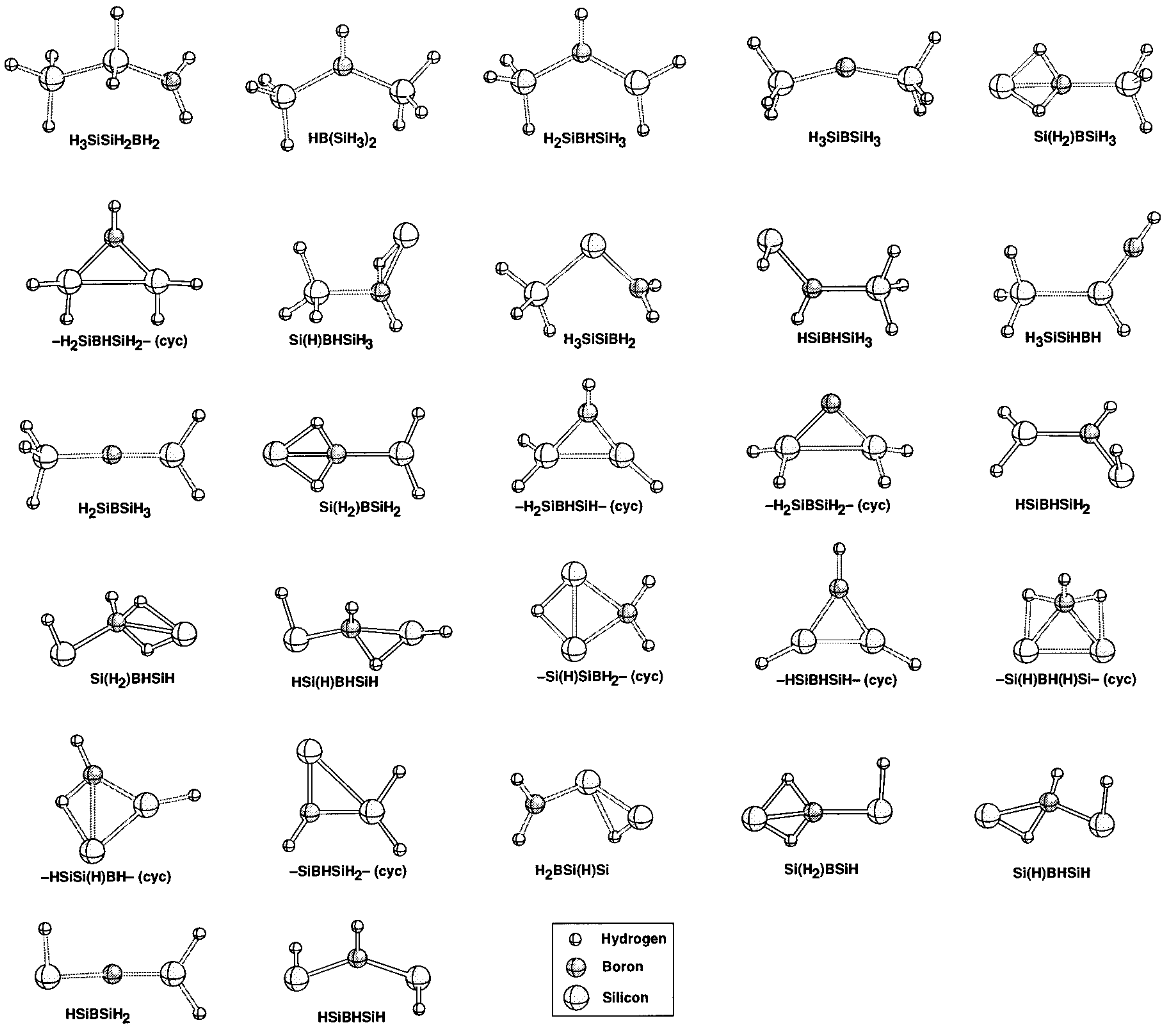

Figure 2. HF/6-31G* structures for Si_2BH_n compounds.

stable Si(H)B species; attempts to find such a structure resulted in SiBH. We note that Mains et al.[25] also did not find a bridged Si(H)B species.

Bridge-bonded Si(H)B groups are not the same in all molecules. For example, $Si(H_2)BH_2$ and $Si(H_2)BHCl$ have calculated Si−B bond lengths of 2.198 and 2.212 Å, respectively, which are longer than the "normal" Si−B single bond length of 2.040 Å calculated for H_3SiBH_2. In contrast, $Si(H_2)BH$ and $Si(H_2)BCl$ have calculated bond lengths of 1.811 and 1.813 Å, which are among the shortest Si−B bonds obtained in this study. Note that H_2SiBH, which is planar and can be thought of as containing a "normal" Si−B double bond, has a calculated Si−B bond length of 1.819 Å. In the $Si(H_2)BH_2$ case, we have simultaneously formed a "divalent" silicon interacting with a "tetravalent" boron due to the bridging hydrogens. The bonds on the B are close to tetrahedral, and the bridge bonds lie opposite from each other in a plane with the Si and the B. The Si−H bonds make a 72° angle at the Si, which is even smaller than expected for s^2p^2 electronic configuration, although the bridging B−H bonds make a 98° angle at the B. In the $Si(H_2)BH$ case, we have a short bond distance (1.811 Å) between the Si and the B in addition to the bridged H bonds. The bridging H atoms are both on one side of the Si−B bond with the H on the B in line with the Si and B.

The presence of Cl on the Si or B does not prevent the formation of bridged H bonds, although, as will be discussed in section III.B, it does affect relative energies of bridged and nonbridged isomers. Bridge-bonded Cl atoms, however, are uncommon. $HSi(HCl)BH_2$ is the only stable species we found that had a bridged Cl atom. The Si−Cl bond distance of 2.29 Å is somewhat longer than normal (2.08 Å in $H_2ClSiBH_2$), as is the B−Cl bond distance of 1.98 Å (1.76 Å in $H_3SiBHCl$). The transition state for the $H_2ClSiBH_2 \rightarrow SiH_2 + BH_2Cl$ reaction also has a bridged Cl atom transferring from the Si to the B. All other attempts to find bridged Cl atoms (which concentrated on the less-saturated species) resulted in the Cl being bonded to either the Si or B. We note that Bock et al.[24] reported a stable species, $FSi(F_2)BH_2$, with bridged F atoms.

Another noteworthy feature in the Si−B−H−Cl compounds is the prevalence of Si−H bonds that are nearly perpendicular to the Si−B bond rather than having a tetrahedral bonding, particularly in the unsaturated molecules. For example, the H−Si−B bond angle is 91.6° in $HSiBH_2$, 88.6° in HSiBH, and 85.8° in HSiB. These nearly perpendicular angles result from the preference of Si atoms in silylenes to have s^2p^2 electronic configuration rather than sp^3 hybridization, as evidenced by the 93.3° bond angle we obtain for SiH_2.

We examine the bonding in $Si_1B_1H_1$ species in more detail. We find SiBH $^3\Sigma^-$ and $^1\Delta$ both to be linear with Si−B bond lengths of 1.86 and 1.88 Å, respectively, indicating the presence of Si−B double bonds and sp hybridization for the B−H bond. For HSiB, we find that the $^3A''$ state has a bond angle close to 90° and a Si−B bond length of 1.935 Å, indicating a nearly single Si−B bond involving an s^2p^2 Si. In contrast, HSiB $^1\Sigma$ (which is not included in our tables because it has a very high energy and was very UHF unstable) is linear with a Si−B bond length of 1.64 Å, indicating a Si−B triple bond. Our attempts to find a bent HSiB singlet were not successful, as the H

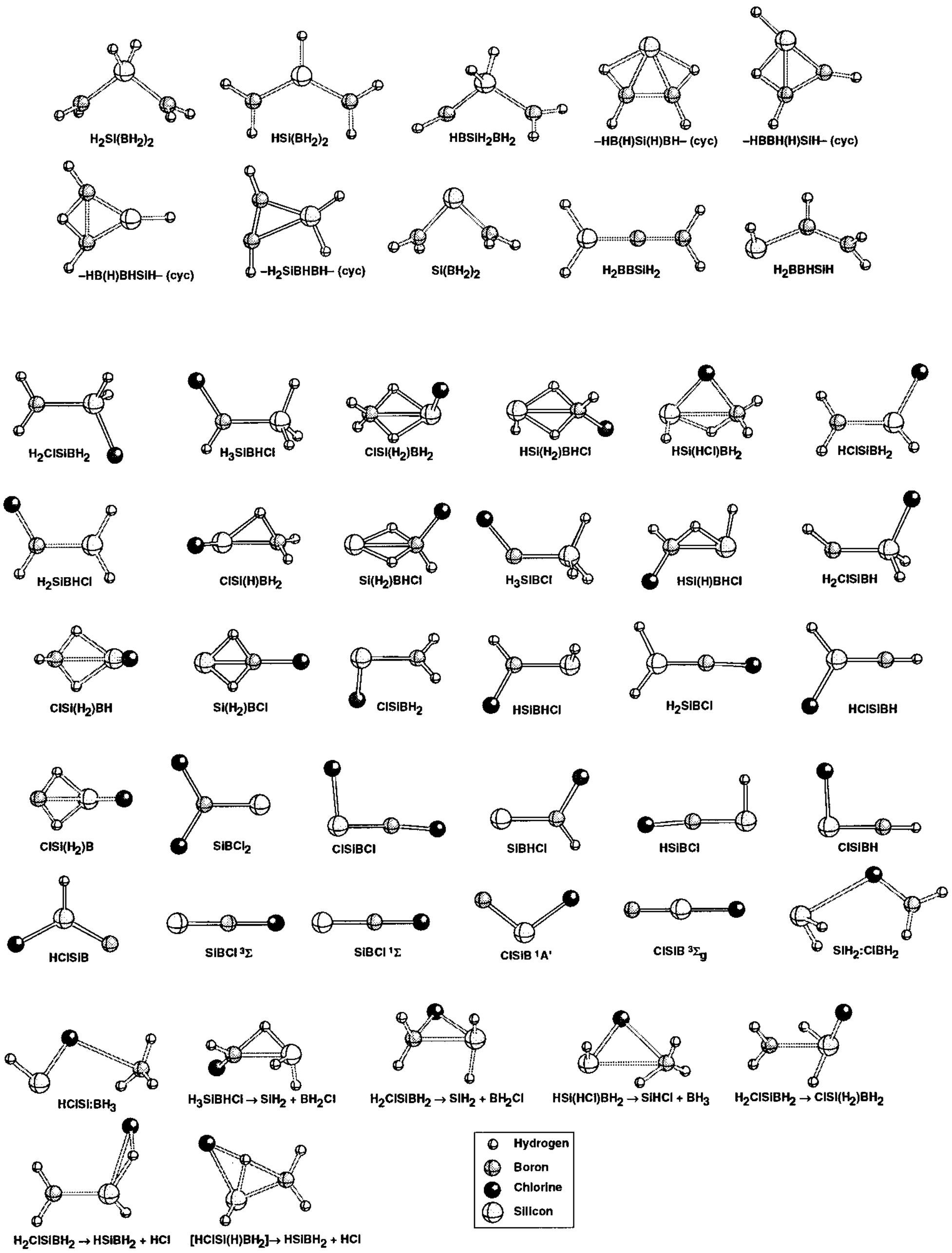

Figure 3. HF/6-31G* structures for SiB_2H_n (top) and $SiBH_nCl_m$ (bottom) compounds.

migrated via a bridged structure to the B atom. We note that we did find a stable bent ClSiB singlet, as the Cl does not form a bridged structure and thus did not migrate to the B. Luke et al.[28] reported similar results for the SiBH species and the bent HSiB triplet, although their energy splittings are greater than ours. They also reported that all linear HSiB species had imaginary frequencies at their level of theory and that a bent HSiB $^1A'$ that was stable with the 3-21G basis set collapsed to SiBH $^1\Delta$ with the 3-21G* basis set. Mains et al.[25] reported a bent $^3A'$ excited state for SiBH as well as the $^3\Sigma^-$ and $^1\Delta$ states. For HSiB, however, they reported a high-energy linear HSiB $^1\Sigma^+$, but no bent triplet.

The presence of Cl on B does not affect the tendency toward perpendicular H−Si−B bonds. This angle is 91.7° in HSiBHCl, 88.1° in HSiBCl, and 90.9° in $HSi(H_2)BHCl$. However, Si−Cl bonds do not exhibit this as cleanly, with Cl−Si−B bond angles ranging from 92.0° in $ClSiBH_2$, 95.2° in ClSiBH, to 106.6° in ClSiB, i.e., intermediate between the perpendicular s^2p^2 and tetrahedral sp^3. For comparison, the calculated Cl−Si−Cl bond angle in $SiCl_2$ is 101.4°.

For the larger Si_2BH_n and SiB_2H_n molecules, we found a number of cyclic species, especially among the unsaturated molecules. In some cases, such as $-H_2SiBHSiH-$ (cyc) or −HSiBHSiH− (cyc), all the bond lengths fall in the “normal” range. In other cases, namely $-H_2SiBHSiH_2-$ (cyc), $-H_2SiBSiH_2-$ (cyc), and $-SiBHSiH_2$- (cyc), the Si−Si bond is much longer than normal, ≥2.6 Å. This indicates the interaction between the two silicon atoms is much weaker than a single bond (for comparison, the Si−Si bond length in Si_2H_6 is 2.35 Å) and that the structure may be more correctly thought of as “pseudocyclic” rather than “cyclic”.

The most unusual geometries, however, are those that combine cyclic structures with bridged H bonds in compounds such as $-Si(H)SiBH_2-$ (cyc), −Si(H)BH(H)Si− (cyc), or −HB(H)Si(H)BH− (cyc). The planarity of $-Si(H)SiBH_2-$ (cyc), −HSiSi(H)BH− (cyc), and −HB(H)Si(H)BH− (cyc) is quite interesting. As in aromatic hydrocarbons, there are delocalized bonds encouraging this planarity. The papers by Subramanian and co-workers[31,32] contain discussions of the bonding in the Si_2BH_3 and SiB_2H_4 molecules.

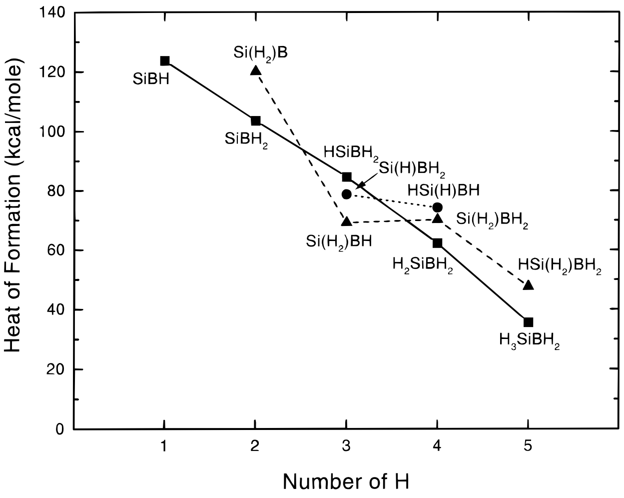

Figure 4. Calculated heats of formation for $SiBH_n$ ($n \leq 5$) compounds as a function of n: squares, no bridged hydrogens (normal isomers); circles, one bridged hydrogen; triangles, two bridged hydrogens. Lines have been drawn between points to guide the eye.

B. Thermochemistry. Table 3 lists calculated $\Delta H°_f(0)$s at various levels of theory for the Si−B−H−Cl species. The substantial differences between the MP4 values and the BAC-MP4 values illustrate the need for corrections such as the BAC or isodesmic reaction[46] methods with these levels of theory. Table 4 gives calculated values for $\Delta H°_f(298)$ at the BAC-MP4 level of theory with error estimates derived from the lower levels of theory. Table 4 also lists calculated heats of formation for a number of other species that either are used in analyzing bond dissociation enthalpies and molecular decomposition reactions or provide comparisons between our calculated values and experimental data. Table 5 collects the calculated heats of formation at 0 and 298 K with entropies and free energies for a range of temperatures. In these tables, the molecules are grouped as follows: first the $SiBH_n$ molecules, then the Si_2BH_n molecules, the SiB_2H_n molecules, and last the $SiBH_nCl$ molecules. Within each group, the species are placed in order of decreasing n, with transition states listed last. For a given n, the most stable isomer is given first with other isomers following in order of increasing $\Delta H°_f$.

The thermochemical data in the literature for Si−B−H−Cl compounds are limited to Si−H−Cl and B−H−Cl species. As shown at the bottom of Table 4, our calculated heats of formation generally agree well with the literature values, although there often are large uncertainties in the latter. These species are only of secondary interest in this paper and have been covered in detail elsewhere.[12,20] As mentioned above, the literature does have electronic structure calculations for some molecules with a Si−B bond, but these studies[21−32] generally emphasize total electronic energies or relative energies, rather than thermochemical data.

The heats of formation in Table 4 exhibit a few noteworthy trends. For the unsaturated molecules, it is generally more favorable to have H (or Cl) bonded to B rather than to Si. For example, H_3SiBH is 23 kcal mol^{-1} less stable than H_2SiBH_2, triplet HSiB is 36 kcal mol^{-1} above triplet SiBH, and singlet HSiB (not included in our tables) is 95 kcal mol^{-1} above singlet SiBH.

Trends in relative stability between the normal and bridge-bonded isomers of various Si−B−H−Cl compounds are somewhat complicated. Figure 4 shows our calculated heats of formation for the $SiBH_n$ species as a function of n for (1) the most stable isomers with a classical structure, (2) the most stable isomers with one bridged H bond, and (3) the most stable isomers with two bridged H bonds. Generally, the bridge-bonded isomers are less stable than normal isomers, except for $n = 3$. Figures 5 and 6 are similar plots for the $SiBH_{n-1}Cl$ ($n \leq 5$) species with Cl on the B and the Si, respectively. These figures make it clear that $Si(H_2)BH$ and $Si(H_2)BCl$ have extra stabilization.

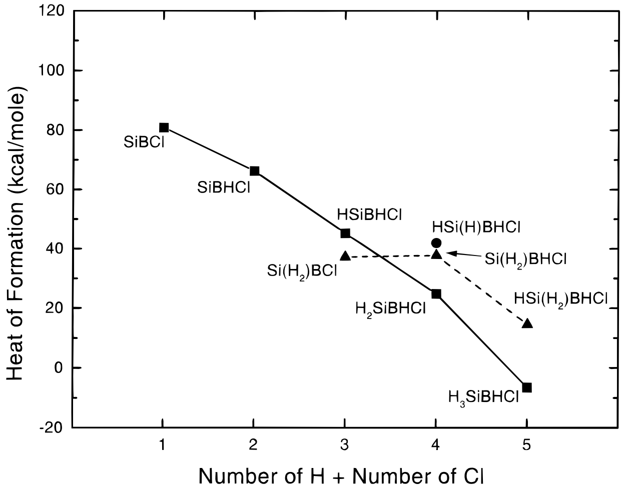

Figure 5. Calculated heats of formation for $SiBH_{n-1}Cl$ ($n \leq 5$) compounds with the Cl bonded to the B as a function of n: squares, no bridged hydrogens (normal isomers); circles, one bridged hydrogen; triangles, two bridged hydrogens. Lines have been drawn between points to guide the eye.

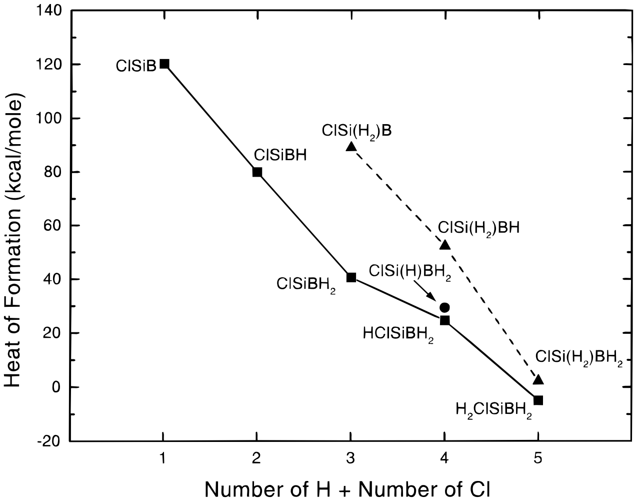

Figure 6. Calculated heats of formation for $SiBH_{n-1}Cl$ ($n \leq 5$) compounds with the Cl bonded to the Si as a function of n: squares, no bridged hydrogens (normal isomers); circles; one bridged hydrogen; triangles, two bridged hydrogens. Lines have been drawn between points to guide the eye.

A comparison of Figures 4 and 5 shows that Cl substitution on the boron raises the enthalpy of the bridged isomers relative to the normal isomers. For example, $HSi(H_2)BH_2$ is 12.0 kcal mol^{-1} above H_3SiBH_2, while $HSi(H_2)BHCl$ is 21.1 kcal mol^{-1} above $H_3SiBHCl$. For $n = 3$, however, the bridged isomers are more stable than the normal isomers, so this Cl substitution brings the bridged and normal isomers closer in energy. $HSiBH_2$ is 15.4 kcal mol^{-1} above $Si(H_2)BH$, while HSiBHCl is only 8.0 kcal mol^{-1} above $Si(H_2)BCl$. $Si(H)BH_2$ is 5.9 kcal mol^{-1} below $HSiBH_2$, while the Cl-substituted analogue, Si(H)BHCl, was not a minimum at our level of theory but rather opened up to HSiBHCl.

In contrast, comparing Figures 4 and 6 shows that Cl substitution on the Si appears to lower the enthalpy of the bridged isomers relative to the normal isomers. For example,

TABLE 3: Calculated ΔH_f° at 0 K for Si−B−H−Cl Compounds at Various Levels of Theory (kcal mol^{-1})

				BAC-MP4	
species	MP4	BAC-MP2	BAC-MP3	SDQ	SDTQ
H_3SiBH_2	64.7	38.6	38.6	38.6	38.6
$HSi(H_2)BH_2$	77.5	52.5	52.7	52.0	51.0
H_2SiBH_2	86.4	63.2	63.9	64.1	63.9
$Si(H_2)BH_2$	95.0	73.1	74.2	73.5	72.6
$HSi(H)BH_2$	99.4	76.7	77.7	77.3	76.3
H_3SiBH	110.7	85.4	86.4	86.8	87.0
$HSi(H_2)BH$	125.6	101.7	102.6	102.4	101.6
$Si(H_2)BH$	91.2	71.2	71.8	72.3	70.7
$Si(H)BH_2$	98.8	81.9	81.2	81.0	79.9
$HSiBH_2\ ^1A'$	105.3	87.8	86.7	86.2	85.8
$H_2SiBH\ ^1A_1$	117.4	95.6	95.0	95.4	94.5
$HSiBH_2\ ^3A''$	114.0	95.6	96.8	97.0	96.8
$H_2SiBH\ ^3A''$	130.7	108.9	110.1	110.8	110.9
H_3SiB	147.0	123.4	121.8	121.0	120.7
$Si(H_3)B$	144.9	123.9	124.5	124.6	122.4
$SiBH_2$	116.4	105.3	104.8	104.5	104.1
$HSiBH$	130.5	116.9	116.6	116.5	115.7
$Si(H_2)B$	140.5	119.6	121.4	121.6	120.4
H_2SiB	162.5	147.6	147.2	147.1	145.5
$SiBH\ ^3\Sigma^-$	134.0	123.4	123.3	124.0	123.5
$SiBH\ ^1\Delta$	151.9	135.0	133.2	132.9	131.9
$HSiB\ ^3A''$	171.0	160.5	160.4	160.6	159.7
SiB	208.4	187.7	189.5	189.0	187.8
$H_3SiBH_2 \rightarrow SiH_2 + BH_3$	104.4	74.7	75.5	75.4	73.2
$H_3SiBH_2 \rightarrow HSiBH_2 + H_2$	110.4	82.8	84.1	85.0	83.3
$HSiBH_2 \rightarrow Si(H)BH_2$	100.3	83.9	83.1	82.8	81.8
$Si(H)BH_2 \rightarrow Si(H_2)BH$	96.7	79.2	79.0	79.0	77.8
$H_3SiSiH_2BH_2$	90.4	48.7	49.1	49.2	49.0
$HB(SiH_3)_2$	95.2	51.7	51.8	51.8	51.7
$H_2SiBHSiH_3$	115.1	74.5	75.4	75.7	75.3
$H_3SiBSiH_3$	137.7	95.1	95.7	95.9	96.2
$Si(H_2)BSiH_3$	116.6	78.7	80.1	80.7	78.8
$-H_2SiBHSiH_2-$ (cyc)	121.1	81.7	84.3	85.3	82.4
$Si(H)BHSiH_3$	121.6	87.1	87.7	87.8	86.0
$H_3SiSiBH_2$	127.2	94.2	94.1	94.0	92.8
$HSiBHSiH_3$	133.0	98.4	97.7	97.3	96.6
$H_3SiSiHBH$	138.8	100.5	100.7	101.3	100.0
$H_2SiBSiH_3$	142.7	102.8	102.6	103.0	101.9
$Si(H_2)BSiH_2$	147.6	112.8	115.0	115.6	113.7
$-H_2SiBHSiH-$ (cyc)	153.4	114.6	115.9	115.6	114.9
$-H_2SiBSiH_2-$ (cyc)	168.7	127.2	130.2	131.0	129.2
$HSiBHSiH_2$	162.2	128.9	129.7	129.5	128.8
$Si(H_2)BHSiH$	174.3	141.3	142.9	142.0	140.5
$HSi(H)BHSiH$	178.0	143.9	145.3	144.7	143.3
$-Si(H)SiBH_2-$ (cyc)	130.4	99.7	103.6	104.5	99.3
$-HSiBHSiH-$ (cyc)	139.2	100.9	103.2	104.7	102.3
$-Si(H)BH(H)Si-$ (cyc)	137.8	107.1	109.7	109.9	106.0
$-HSiSi(H)BH-$ (cyc)	139.3	106.8	109.2	109.8	106.3
$-SiBHSiH_2-$ (cyc)	142.7	110.4	113.3	114.4	109.9
$H_2BSi(H)Si$	148.4	122.4	122.5	122.7	119.8
$Si(H_2)BSiH$	160.2	130.3	131.0	131.3	128.8
$Si(H)BHSiH$	166.0	139.0	138.4	137.9	135.7
$HSiBSiH_2$	170.6	140.6	140.2	140.3	137.7
$HSiBHSiH$	171.9	145.6	144.0	143.2	141.8
$H_2Si(BH_2)_2$	97.7	64.7	65.0	65.0	64.9
$HSi(BH_2)_2$	114.1	84.0	84.9	85.2	85.0
$HBSiH_2BH_2$	143.9	111.8	113.0	113.4	113.5
$-HB(H)Si(H)BH-$ (cyc)	97.7	65.7	70.4	70.7	67.4
$-HBBH(H)SiH-$ (cyc)	113.1	78.5	84.0	84.6	81.5
$-HB(H)BHSiH-$ (cyc)	116.2	83.7	88.5	89.8	86.3
$-H_2SiBHBH-$ (cyc)	119.7	87.0	92.0	91.6	88.2
$Si(BH_2)_2$	122.6	99.9	100.2	100.0	98.4
H_2BBSiH_2	132.9	104.0	105.2	105.4	103.8
$H_2BBHSiH$	130.6	107.9	108.1	107.7	106.9
$H_3SiBHCl$	24.3	−3.6	−3.5	−3.7	−3.9
$H_2ClSiBH_2$	30.1	−2.8	−2.2	−2.2	−2.5
$ClSi(H_2)BH_2$	37.5	6.6	7.8	7.0	5.1
$HSi(H_2)BHCl$	45.7	18.8	19.4	18.7	17.5
$HSi(HCl)BH_2$	49.4	21.7	23.4	21.7	19.1
$HClSiBH_2$	55.1	25.6	26.7	26.6	26.1
$H_2SiBHCl$	50.6	25.8	26.7	26.7	26.3
$ClSi(H)BH_2$	60.6	31.7	33.5	32.6	31.0
$Si(H_2)BHCl$	63.8	40.1	41.6	40.9	39.7

TABLE 3 (Continued)

species	MP4	BAC-MP2	BAC-MP3	BAC-MP4	
				SDQ	SDTQ
H_3SiBCl	69.1	42.4	43.0	43.1	43.1
$HSi(H)BHCl$	68.8	44.2	45.4	44.7	43.7
$H_2ClSiBH$	75.6	43.6	45.1	45.5	45.4
$ClSi(H_2)BH$	84.0	54.2	56.2	55.8	54.0
$Si(H_2)BCl$	60.6	38.8	39.4	39.7	38.2
$ClSiBH_2$	65.9	43.2	43.5	42.8	41.3
$HSiBHCl$	67.6	48.1	47.3	46.7	46.0
H_2SiBCl	74.9	50.1	49.2	49.2	47.6
$HClSiBH$	89.3	57.8	57.3	57.8	56.8
$ClSi(H_2)B$	121.2	93.7	93.7	92.7	90.0
$SiBCl_2$	41.9	27.2	27.9	27.1	26.3
$ClSiBCl$	59.4	36.0	36.9	36.0	34.5
$SiBHCl$	80.4	67.6	67.5	67.0	66.4
$HSiBCl$	87.2	72.0	71.2	71.0	70.0
$ClSiBH$	101.8	80.1	81.5	80.9	79.7
$HClSiB$	131.6	110.9	110.8	110.3	108.1
$SiBCl\ ^3\Sigma$	93.2	80.9	80.4	80.8	80.2
$SiBCl\ ^1\Sigma$	109.8	91.1	89.2	88.7	87.3
$ClSiB\ ^1A'$	149.6	126.6	127.6	126.1	119.4
$ClSiB\ ^3\Sigma^-$	175.7	151.2	153.0	153.6	152.4
$HClSi{:}BH_3$	64.8	40.8	40.5	39.8	38.6
$H_2Si{:}BH_2Cl$	67.5	47.9	46.5	46.1	45.6
$H_3SiBHCl \rightarrow SiH_2 + BH_2Cl$	67.1	36.2	37.7	37.4	34.8
$H_2ClSiBH_2 \rightarrow SiH_2 + BH_2Cl$	77.4	41.4	43.2	42.0	38.2
$HSi(HCl)BH_2 \rightarrow SiHCl + BH_3$	61.6	38.1	39.0	37.5	35.2
$H_2ClSiBH_2 \rightarrow ClSi(H_2)BH_2$	79.8	45.4	46.4	46.4	44.0
$H_2ClSiBH_2 \rightarrow HSiBH_2 + HCl$	99.4	68.5	71.5	71.2	68.0
$[HClSi(H)BH_2] \rightarrow HSiBH_2 + HCl$	99.1	72.7	75.7	75.2	71.2

$ClSi(H_2)BH_2$ is only 7.1 kcal mol^{-1} above $H_2ClSiBH_2$, whereas $HSi(H_2)BH_2$ is 12.0 kcal mol^{-1} above H_3SiBH_2. However, the number of directly analogous molecules available for making such comparisons is very limited in this case.

Although the data are again limited, it also appears that silyl substitution on the B may lower the bridged isomers relative to the normal isomers. $Si(H_2)BSiH_3$ is 18.0 kcal mol^{-1} below $HSiBHSiH_3$, which is somewhat larger than the 15.4 kcal mol^{-1} separation between $Si(H_2)BH$ and $HSiBH_2$.

C. Bond Dissociation Enthalpies. Table 6 lists bond dissociation enthalpies (BDEs) for Si−H, Si−Cl, B−H, B−Cl, and Si−B bonds obtained from the heats of formation in Table 4. Related molecules have been grouped to illustrate trends and patterns in the BDEs. A few BDEs for Si−H−Cl and B−H−Cl compounds are included for comparison. Generally, only simple bond dissociation reactions involving the ground electronic state are included. Reactions involving a major rearrangement of the molecule are not included, i.e., reactions involving the interconversion of bridged and nonbridged species or cyclic and noncyclic species. Caution should thus be exercised in cases where the most stable isomer is a bridged or cyclic species. A few cases are included where the dissociation of a bridged species leads to a H atom and a new species with one fewer bridged bonds, as this is viewed as the dissociation of the three-center bond.

The BDEs in Table 6 for a given bond type vary significantly, although there are some notable trends. Overall, Si−H bonds are weaker than Si−Cl bonds, and B−H bonds are weaker than B−Cl bonds, as expected from BDEs in simpler molecules. Si−B bonds are of the same magnitude as Si−H bonds, and Si−Cl bonds are of the same magnitude as B−H bonds. BDEs for bridged H atoms are closer in magnitude to Si−H BDEs rather than B−H BDEs and have been placed in the table accordingly. They are also close to BDEs for bridged H bonds in Si compounds. The ΔH's for $Si(H_2)Si \rightarrow Si(H)Si + H$ and $Si(H)Si \rightarrow Si_2 + H$ BDEs are 75.3 and 74.3 kcal mol^{-1}, respectively.

In many cases, BDEs involving species with bridge bonds are nearly the same as BDEs for species with the same number of nonbridged Si−H bonds. For example, the $H-Si(H_2)BH_2$ and $H-SiH_2BH_2$ BDEs are 74.7 and 78.7 kcal mol^{-1}, and the $H-BH(H_2)SiCl$ and $H-BHSiH_2Cl$ BDEs are 102.2 and 100.8 kcal mol^{-1}, respectively. In other cases, there are large differences. In particular, the dissociation of species that results in the formation of $Si(H_2)BH$ and $Si(H_2)BCl$ have exceptionally low BDEs as a result of the extreme stability of these dibridged species. For example, the $H-Si(H_2)BH$ and $HSi-BH(H_2)Si$ BDEs are only 22 kcal mol^{-1}, while other Si−H and Si−B BDEs are in the range 50−90 kcal mol^{-1}.

Substituting larger groups for H affects BDEs in the Si−B−H−Cl species in a variety of ways. In the saturated compounds, substituting a BH_2 group for a H on the Si decreases the Si−X (X = H, Cl) BDEs. The $H-SiH_3$, $H-SiH_2BH_2$, and $H-SiH(BH_2)_2$ BDEs decrease from 91.3, to 78.7, to 73.1 kcal mol^{-1}, and the $Cl-SiH_3$ and $Cl-SiH_2BH_2$ BDEs drop from 108.4 to 96.1 kcal mol^{-1}. Note that this results in Si−H bonds that are considerably weaker than those in analogous molecules. For example, multiple NH_2-for-H[15] and CH_3-for-H[16] substitutions increase the Si−H BDEs in the saturated compounds from 91.3 kcal mol^{-1} to 98.2 and 94.6 kcal mol^{-1}, respectively. The unsaturated Si−B−H−Cl compounds show a pattern that differs from both the saturated Si−B−H−Cl compounds and other unsaturated silicon compounds. The $H-SiH_2$, $H-SiHBH_2$, and $H-Si(BH_2)_2$ BDEs are 69.5, 74.5, and 66.3, respectively, and the BDEs for $Cl-SiH_2$ and $Cl-SiH_2BH_2$ increase from 85.9 to 89.0 kcal mol^{-1}. For comparison, the $H-SiH_2$, $H-SiHCH_3$, and $H-Si(CH_3)_2$ BDEs decrease from 69.5, to 67.9, to 66.0 kcal mol^{-1}, respectively.[16] Substitutions on the B also alter B−H BDEs in a manner reminiscent of the effect BH_2-for-H substitutions had on Si−H BDEs. The $H-BH_2$, $H-BHSiH_3$, and $H-B(SiH_3)_2$ BDEs decrease from 105.3, to 101.4, to 97.4 kcal mol^{-1}, while the $H-BH$ and $H-BSiH_3$ BDEs increase from 78.9 to 86.7 kcal mol^{-1}.

TABLE 4: Calculated Heats of Formation at 298 K from the BAC-MP4(SDTQ) Level of Theory, with Error Estimates,[a] (kcal mol^{-1}) and Previously Published Comparisons with Literature for Related Species

species	calc ΔH_f°	error est[a]	species	calc ΔH_f°	error est[a]
H_3SiBH_2[b]	35.6	1.0	$H_3SiBHCl$	−6.6	1.1
$HSi(H_2)BH_2$	47.6	2.2	$H_2ClSiBH_2$	−4.9	1.1
H_2SiBH_2	62.2	1.0	$ClSi(H_2)BH_2$	2.2	3.5
$Si(H_2)BH_2$	70.2	2.2	$HSi(H_2)BHCl$	14.5	2.4
$HSi(H)BH_2$	74.2	1.9	$HSi(HCl)BH_2$	16.4	5.1
H_3SiBH	84.9	1.2	$HClSiBH_2$	24.6	1.3
$HSi(H_2)BH$	99.3	1.6	$H_2SiBHCl$	24.8	1.1
$Si(H_2)BH$	69.2	2.1	$ClSi(H)BH_2$	29.3	3.2
$Si(H)BH_2$	78.7	2.0	$Si(H_2)BHCl$	37.7	2.4
$HSiBH_2\ ^1A'$	84.6	1.6	H_3SiBCl	41.4	1.0
$H_2SiBH\ ^1A_1$	93.4	1.5	$HSi(H)BHCl$	41.9	2.2
$HSiBH_2\ ^3A''$	95.5	1.0	$H_2ClSiBH$	43.8	1.0
$H_2SiBH\ ^3A''$	109.8	1.2	$ClSi(H_2)BH$	52.3	2.9
H_3SiB	119.5	2.0	$Si(H_2)BCl$	37.2	2.1
$Si(H_3)B$	120.7	3.3	$ClSiBH_2$	40.6	2.8
$SiBH_2$	103.6	1.3	$HSiBHCl$	45.2	1.9
$HSiBH$	115.6	1.5	H_2SiBCl	47.1	2.6
$Si(H_2)B$	120.0	2.0	$HClSiBH$	56.1	1.9
H_2SiB	145.3	2.5	$ClSi(H_2)B$	89.0	4.9
$SiBH\ ^3\Sigma^-$	123.7	1.1	$SiBCl_2$	26.6	2.1
$SiBH\ ^1\Delta$	132.1	2.8	$ClSiBCl$	35.2	3.1
$HSiB\ ^3A''$	160.2	1.5	$SiBHCl$	66.2	1.6
SiB	188.8	3.5	$HSiBCl$	70.2	1.9
$H_3SiBH_2 \rightarrow SiH_2 + BH_3$	70.1	3.5	$ClSiBH$	79.9	2.4
$H_3SiBH_2 \rightarrow HSiBH_2 + H_2$	80.3	2.1	$HClSiB$	108.3	3.6
$HSiBH_2 \rightarrow Si(H)BH_2$	80.4	1.9	$SiBCl\ ^3\Sigma$	80.9	1.2
$Si(H)BH_2 \rightarrow Si(H_2)BH$	76.1	2.1	$SiBCl\ ^1\Sigma$	88.1	3.2
			$ClSiB\ ^1A'$	120.2	11.0
$H_3SiSiH_2BH_2$	44.8	1.0	$ClSiB\ ^3\Sigma^-$	152.9	1.8
$HB(SiH_3)_2$	47.4	1.0	$HClSi{:}BH_3$	37.3	2.6
$H_2SiBHSiH_3$	71.9	1.1	$H_2Si{:}BH_2Cl$	44.1	1.5
$H_3SiBSiH_3$	92.7	1.2	$H_3SiBHCl \rightarrow SiH_2 + BH_2Cl$	32.1	4.0
$Si(H_2)BSiH_3$	75.9	2.4	$H_2ClSiBH_2 \rightarrow SiH_2 + BH_2Cl$	35.5	6.4
$-H_2SiBHSiH_2-$ (cyc)	79.4	3.6	$HSi(HCl)BH_2 \rightarrow SiHCl + BH_3$	32.7	4.6
$Si(H)BHSiH_3$	83.1	2.7	$H_2ClSiBH_2 \rightarrow ClSi(H_2)BH_2$	41.6	3.6
$H_3SiSiBH_2$	90.0	2.2	$H_2ClSiBH_2 \rightarrow HSiBH_2 + HCl$	65.7	4.9
$HSiBHSiH_3$	93.9	1.8	$[HClSi(H)BH_2] \rightarrow HSiBH_2 + HCl$	68.8	6.0
$H_3SiSiHBH$	97.3	1.9			
$H_2SiBSiH_3$	99.2	1.8	$H_2Si(BH_2)_2$	61.6	1.0
$Si(H_2)BSiH_2$	111.7	2.5	$HSi(BH_2)_2$	82.6	1.0
$-H_2SiBHSiH-$ (cyc)	112.8	1.6	$HBSiH_2BH_2$	111.1	1.2
$-H_2SiBSiH_2-$ (cyc)	127.0	2.4	$-HB(H)Si(H)BH-$ (cyc)	65.1	4.6
$HSiBHSiH_2$	127.2	1.7	$-HBBH(H)SiH-$ (cyc)	79.3	4.2
$Si(H_2)BHSiH$	138.3	3.2	$-HB(H)BHSiH-$ (cyc)	84.0	4.2
$HSi(H)BHSiH$	141.5	2.8	$-H_2SiBHBH-$ (cyc)	86.5	5.2
$-Si(H)SiBH_2-$ (cyc)	98.0	6.8	$Si(BH_2)_2$	96.8	2.5
$-HSiBHSiH-$ (cyc)	100.7	2.7	H_2BBSiH_2	102.2	2.4
$-Si(H)BH(H)Si-$	104.2	5.5	$H_2BBHSiH$	105.3	1.8
$-HSiSi(H)BH-$ (cyc)	105.2	4.7			
$-SiBHSiH_2-$ (cyc)	109.0	5.7			
$H_2BSi(H)Si$	118.6	4.1			
$Si(H_2)BSiH$	127.6	3.6			
$Si(H)BHSiH$	134.6	3.7			
$HSiBSiH_2$	136.8	3.9			
$HSiBHSiH$	140.9	3.0			

species	calc ΔH_f°	lit. ΔH_f° [c]	species	calc ΔH_f°	lit. ΔH_f° [c]
SiH_4[b]	8.2	8.2, 8.3	Si_2H_6[b]	19.1	19.1
SiH_3	47.4	46.4−48.5,[d] 54.2	H_2SiSiH_3	55.4	53.3
SiH_2	64.8	63.6−69.1[d]	$HSiSiH_3$	74.9	74.6[e]
SiH	91.0	90.0	Si_3H_8	28.4	28.9
SiH_3Cl	−32.0	−33.9 − −48.0			
SiH_2Cl_2	−74.4	−76.6 − −80.0	BH_3[b]	22.4	21−25.5
$SiHCl_3$	−117.1	−115.1 − −118.6	BH_2	75.6	45.7−76.1
$SiCl_4$[b]	−158.4	−158.4	BH	102.4	105.8−108.2
$SiCl_3$	−76.0	−75.5 − −93.3	BH_2Cl	−20.3	−19.3
$SiCl_2$	−36.2	−39.5 − −40.3	$BHCl$	32.2	31.3
$SiCl$	37.8	37[f]−47.4	BCl_3[b]	−96.7	−96.6 − −97.5
SiH_2Cl	7.9		BCl_2	−7.5	−14.6, −19
$SiHCl$	15.8		BCl	43.7	33.8−41.2
HCl	−22.0	−22.06	B	134.9	
Si	107.4				
H	52.1				
Cl	29.0				

[a] See section II for discussion of error estimates. [b] Reference compound for BAC. [c] See refs 12−14, 20, and/or 42 for discussions of most of the literature values. [d] See: Jasinski, J. M.; Becerra, R.; Walsh, R. *Chem. Rev.* **1995**, *95*, 1203. [e] See: Becerra, R.; Walsh, R. *J. Phys. Chem.* **1987**, *91*, 5765. [f] See: Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 2233.

TABLE 5: Calculated Thermochemical Parameters at Various Temperatures (K)

	ΔH_f° [a]			ΔG_f° [a]					
species	0 K	298 K	S° [b]	300 K	600 K	1000 K	1500 K	2000 K	2500 K
H_3SiBH_2	38.6	35.6	67.2	40.5	45.8	54.1	63.9	75.8	89.2
$HSi(H_2)BH_2$	51.0	47.6	61.4	54.3	62.0	73.8	88.2	104.7	122.7
H_2SiBH_2	63.9	62.2	67.3	62.4	63.1	65.0	67.0	71.3	77.3
$Si(H_2)BH_2$	72.6	70.2	60.6	72.4	75.5	81.1	87.9	97.0	107.8
$HSi(H)BH_2$	76.3	74.1	62.8	75.7	78.0	82.0	86.8	93.9	102.6
H_3SiBH	87.0	84.9	67.9	84.9	85.2	86.4	87.7	91.2	96.3
$HSi(H_2)BH$	101.6	99.3	62.1	101.1	103.6	108.1	113.5	121.2	130.5
$Si(H_2)BH$	70.7	69.2	58.4	67.5	66.3	65.9	65.4	67.4	71.2
$Si(H)BH_2$	79.9	78.7	60.4	76.3	74.4	72.9	70.8	71.3	73.5
$HSiBH_2$ $^1A'$	85.8	84.6	61.1	82.1	79.9	77.8	75.0	74.8	76.4
H_2SiBH $^1A_1$	94.5	93.4	59.8	91.2	89.4	87.8	85.8	86.2	88.5
$HSiBH_2$ $^3A''$	96.8	95.5	62.3	92.6	90.1	87.7	84.6	84.1	85.5
H_2SiBH $^3A''$	110.9	109.8	63.5	106.5	103.5	100.3	96.1	94.5	94.7
H_3SiB	120.7	119.5	58.8	117.6	116.1	115.0	113.5	114.5	117.2
$Si(H_3)B$	122.4	120.7	58.2	119.0	118.0	117.8	117.5	119.6	123.5
$SiBH_2$	104.1	103.6	58.6	97.2	91.0	83.8	74.9	68.9	64.8
$HSiBH$	115.7	115.6	61.9	108.1	100.8	91.8	80.7	72.2	65.8
$Si(H_2)B$	120.4	120.0	60.4	113.0	106.3	98.1	88.0	80.6	75.1
H_2SiB	145.5	145.3	61.2	138.0	130.9	122.3	111.5	103.5	97.4
$SiBH$ $^3\Sigma^-$	123.5	123.7	54.7	113.7	103.9	91.4	76.0	63.4	52.9
$SiBH$ $^1\Delta$	131.9	132.1	52.3	122.9	113.7	102.3	88.2	76.9	67.7
$HSiB$ $^3A''$	159.7	160.2	59.7	148.7	137.3	123.0	105.2	90.5	77.9
SiB	187.8	188.8	52.1	175.0	161.1	143.5	121.7	103.0	86.5
$H_3SiBH_2 \rightarrow SiH_2 + BH_3$	73.2	70.1	62.7	76.4	83.5	94.5	108.3	124.4	142.3
$H_3SiBH_2 \rightarrow HSiBH_2 + H_2$	83.3	80.3	63.3	86.4	93.4	104.0	117.1	132.5	149.5
$HSiBH_2 \rightarrow Si(H)BH_2$	81.8	80.4	59.5	78.3	76.9	76.3	75.9	78.4	82.9
$Si(H)BH_2 \rightarrow Si(H_2)BH$	77.8	76.1	58.0	74.5	73.6	73.9	74.8	78.4	84.2
$H_3SiSiH_2BH_2$	49.0	44.8	80.8	56.3	68.4	85.6	106.1	130.4	157.3
$HB(SiH_3)_2$	51.7	47.4	83.0	58.2	69.8	86.4	105.9	129.3	155.0
$H_2SiBHSiH_3$	75.3	71.9	80.3	78.9	86.4	97.3	110.2	127.3	146.8
$H_3SiBSiH_3$	96.2	92.7	84.4	98.5	104.8	114.3	125.4	140.7	158.6
$Si(H_2)BSiH_3$	78.8	75.9	74.0	80.1	84.9	92.6	101.6	115.0	131.1
$-H_2SiBHSiH_2-$ (cyc)	82.4	79.4	72.7	84.1	89.3	97.5	107.2	121.3	138.1
$Si(H)BHSiH_3$	86.0	83.1	75.4	86.9	91.5	98.9	107.2	119.8	135.3
$H_3SiSiBH_2$	92.8	90.0	79.2	92.7	95.7	100.9	106.8	117.1	130.4
$HSiBHSiH_3$	96.6	93.9	77.3	97.2	100.8	106.6	113.1	124.0	137.6
$H_3SiSiHBH$	100.0	97.3	77.0	100.7	104.4	110.4	117.3	128.6	142.8
$H_2SiBSiH_3$	101.9	99.2	77.5	102.4	105.9	111.6	118.2	129.2	143.0
$Si(H_2)BSiH_2$	113.7	111.7	74.7	111.1	111.1	112.0	112.7	117.9	126.2
$-H_2SiBHSiH-$ (cyc)	114.9	112.8	1.6	112.8	113.3	114.9	116.5	122.7	131.9
$-H_2SiBSiH_2-$ (cyc)	129.2	127.0	2.4	127.0	127.5	129.1	130.8	137.0	146.3
$HSiBHSiH_2$	128.8	127.2	77.2	125.9	124.9	124.1	122.6	125.8	132.0
$Si(H_2)BHSiH$	140.5	138.3	76.0	137.3	136.6	137.0	137.2	142.0	149.8
$HSi(H)BHSiH$	143.3	141.5	75.8	140.6	140.1	140.2	139.9	144.1	151.3
$-Si(H)SiBH_2-$ (cyc)	99.3	98.0	68.3	94.6	91.7	88.9	85.5	86.9	91.5
$-HSiBHSiH-$ (cyc)	102.3	100.7	67.7	97.5	94.8	92.1	88.7	90.1	94.8
$-Si(H)BH(H)Si-$ (cyc)	106.0	104.2	67.1	101.2	98.8	97.0	94.7	97.3	103.1
$-HSiSi(H)BH-$ (cyc)	106.3	105.2	74.0	100.1	95.4	90.3	83.8	82.2	83.9
$-SiBHSiH_2-$ (cyc)	109.9	109.0	73.7	104.0	99.3	94.2	87.7	86.1	87.8
$H_2BSi(H)Si$	119.8	118.6	72.1	114.1	110.0	105.6	99.8	98.8	101.0
$Si(H_2)BSiH$	128.8	127.5	71.0	123.4	119.6	115.7	110.8	110.6	113.5
$Si(H)BHSiH$	135.7	134.7	72.6	130.0	125.5	120.3	113.6	111.6	112.8
$HSiBSiH_2$	137.7	136.8	73.0	132.0	127.6	122.5	115.9	114.0	115.4
$HSiBHSiH$	141.8	140.9	73.0	136.1	131.6	126.3	119.4	117.2	118.2
$H_2Si(BH_2)_2$	64.9	61.6	77.5	68.6	75.6	86.2	98.4	112.8	129.0
$HSi(BH_2)_2$	85.0	82.6	73.9	86.0	89.8	96.1	103.0	112.3	123.4
$HBSiH_2BH_2$	113.5	111.1	77.6	113.4	115.4	119.2	123.1	129.4	137.5
$-HB(H)Si(H)BH-$ (cyc)	67.4	65.1	65.7	66.3	68.0	71.7	75.9	82.7	91.7
$-HBBH(H)SiH-$ (cyc)	81.4	79.3	66.2	80.3	81.9	85.3	89.0	95.4	103.9
$-HB(H)BHSiH-$ (cyc)	86.3	84.0	65.3	85.3	87.2	91.0	95.3	102.3	111.3
$-H_2SiBHBH-$ (cyc)	88.2	86.5	69.8	86.4	86.8	88.2	89.6	93.5	99.5
$Si(BH_2)_2$	98.4	96.8	70.4	96.5	96.8	97.9	98.8	102.1	107.6
H_2BBSiH_2	103.8	102.2	68.4	102.5	103.3	105.4	107.3	111.9	118.6
$H_2BBHSiH$	106.9	105.3	70.2	105.1	105.2	106.2	107.0	110.3	115.8
$H_3SiBHCl$	−3.9	−6.5	75.0	−0.6	5.6	14.7	25.5	38.4	52.7
$H_2ClSiBH_2$	−2.5	−4.9	73.5	1.4	8.1	17.7	29.2	42.8	57.8
$ClSi(H_2)BH_2$	5.1	2.2	70.1	9.6	17.7	29.8	44.4	61.2	79.4
$HSi(H_2)BHCl$	17.5	14.5	69.4	22.1	30.5	42.9	58.0	75.1	93.7
$HSi(HCl)BH_2$	19.1	16.4	70.1	23.7	31.8	43.5	57.8	74.1	91.9
$HClSiBH_2$	26.1	24.6	72.6	26.5	28.8	32.5	36.8	43.3	51.5
$H_2SiBHCl$	26.3	24.8	72.5	26.8	29.1	32.8	37.0	43.5	51.8
$ClSi(H)BH_2$	31.0	29.3	71.8	31.5	34.1	38.4	43.5	50.8	59.9
$Si(H_2)BHCl$	39.7	37.7	70.1	40.4	43.8	49.4	56.1	65.2	76.0

TABLE 5: (continued)

	$\Delta H_f°$ [a]			$\Delta G_f°$ [a]					
species	0 K	298 K	$S°$ [b]	300 K	600 K	1000 K	1500 K	2000 K	2500 K
H_3SiBCl	43.1	41.4	74.5	42.8	44.3	47.0	50.0	55.3	62.2
$HSi(H)BHCl$	43.7	41.9	71.1	44.3	47.2	51.8	57.2	64.9	74.1
$H_2ClSiBH$	45.4	43.8	72.8	45.7	47.9	51.3	55.0	61.0	68.6
$ClSi(H_2)BH$	54.0	52.3	71.3	54.6	57.4	61.9	67.2	74.9	84.1
$Si(H_2)BCl$	38.2	37.2	66.9	36.2	35.6	35.6	35.5	37.9	42.1
$ClSiBH_2$	41.3	40.6	70.5	38.6	36.7	34.8	32.2	32.3	34.2
$HSiBHCl$	46.0	45.2	69.9	43.4	41.7	40.0	37.7	38.0	40.1
H_2SiBCl	47.6	47.1	70.3	45.0	43.2	41.3	38.8	38.7	40.5
$HClSiBH$	56.8	56.1	71.5	53.8	51.6	49.3	46.3	45.9	47.3
$ClSi(H_2)B$	90.0	89.0	69.3	87.3	85.9	84.8	83.2	84.0	86.6
$SiBCl_2$	26.3	26.6	75.5	21.7	16.7	10.5	2.7	−2.4	−5.4
$ClSiBCl$	34.5	35.2	80.2	28.9	22.4	14.2	3.9	−3.6	−9.2
$SiBHCl$	66.4	66.2	68.9	60.0	53.9	46.6	37.5	31.2	26.9
$HSiBCl$	70.0	70.2	70.0	63.6	57.1	48.9	38.8	31.3	25.8
$ClSiBH$	79.7	79.9	71.0	73.0	66.2	57.6	46.8	38.9	32.9
$HClSiB$	108.1	108.3	70.7	101.5	94.8	86.3	75.7	67.8	62.0
$SiBCl\ ^3\Sigma$	80.2	80.9	63.6	71.6	62.2	50.1	35.2	23.0	13.0
$SiBCl\ ^1\Sigma$	87.4	88.1	61.2	79.5	70.8	59.8	46.0	35.2	26.3
$ClSiB\ ^1A'$	119.4	120.2	66.8	109.9	99.6	86.5	70.3	57.1	46.1
$ClSiB\ ^3\Sigma^-$	152.4	152.9	62.7	143.9	134.9	123.6	109.6	98.4	89.3
$HClSi{:}BH_3$	38.6	37.3	93.6	37.7	38.0	39.0	39.8	42.7	47.0
$H_2Si{:}BH_2Cl$	45.6	44.1	84.7	47.1	50.2	54.9	60.2	67.6	76.4
$H_3SiBHCl \rightarrow SiH_2 + BH_2Cl$	34.8	32.1	71.0	39.2	47.0	58.6	72.8	89.5	107.8
$H_2ClSiBH_2 \rightarrow SiH_2 + BH_2Cl$	38.2	35.5	69.5	43.0	51.2	63.3	78.3	95.8	114.9
$HSi(HCl)BH_2 \rightarrow SiHCl + BH_3$	35.2	32.7	72.4	39.3	46.7	57.8	71.6	87.9	105.8
$H_2ClSiBH_2 \rightarrow ClSi(H_2)BH_2$	44.0	41.6	73.0	48.1	55.2	65.7	78.6	94.0	111.0
$H_2ClSiBH_2 \rightarrow HSiBH_2 + HCl$	68.0	65.7	75.0	71.6	78.0	87.3	98.6	112.2	127.6
$[HClSi(H)BH_2] \rightarrow HSiBH_2 + HCl$	71.2	68.8	72.4	75.5	82.7	93.2	106.2	121.4	138.3

[a] In kcal mol^{-1}. [b] In cal mol^{-1} K^{-1}.

Substituting SiH_3 for H on B had little effect on more distant Si−H BDEs. The $H{-}SiH_2BH_2$ and $H{-}SiH_2BHSiH_3$ BDEs are 78.7 and 76.6 kcal mol^{-1}, and $H{-}SiHBH_2$ and $H{-}SiHBHSiH_3$ are 74.5 and 74.1 kcal mol^{-1}. Likewise, such substitutions had minor effects on Si−B BDEs. The $H_3Si{-}BH_2$, $H_2Si{-}BH_2$, and $HSi{-}BH_2$ BDEs are 87.4, 78.2, and 82.0 kcal mol^{-1}, while the $H_3Si{-}BHSiH_3$, $H_2Si{-}BHSiH_3$, and $HSi{-}BHSiH_3$ have very similar BDEs of 84.9, 77.8, and 82.0 kcal mol^{-1}, respectively.

Cl substitution for H had little effect on Si−B BDEs in saturated compounds. The $H_3Si{-}BH_2$, $H_3Si{-}BHCl$, and $H_2ClSi{-}BH_2$ BDEs are 87.4, 86.2, and 88.4 kcal mol^{-1}, respectively. In contrast, Cl substitution in unsaturated species can weaken the Si−B bond noticeably. The BDEs for HSi−BH, HSi−BCl, ClSi−BH, and ClSi−BCl are 77.8, 64.5, 60.3, and 46.3 kcal mol^{-1}, respectively.

In other silicon compounds, the successive dissociation of Si−X bonds shows a pattern in which the second BDE is substantially lower than the first, and the third BDE is higher than the second.[14] This "high−low−high" pattern results from the change in electronic configuration at SiX_2 from sp^3 to s^2p^2 and is illustrated by the successive Si−H BDEs given at the top of Table 6. Similar behavior has also been observed in the $SiCl_n$, SiF_n, $Si(CH_3)_n$, $Si(NH_2)H_n$, and $Si(NH_2)F_n$ species.[14−18] Successive Si−H BDEs in H_3SiBH_2 do not exhibit this variation, but rather decrease monotonically from 78.7 to 71.1 kcal mol^{-1}. However, this series does not include the most stable isomer of $HSiBH_2$, which is the dibridged structure. Including this species would introduce ∼15 kcal mol^{-1} more variation in Si−H BDEs, but the concept of successive Si−H bonds becomes poorly defined when the bridged structures are included. The trend of alternating high and low BDEs does appear in the less saturated species and when the number of H atoms bonded to the B is varied.

D. Reactions. Table 7 lists $\Delta H°_{rxn}(298)$ for various decomposition reactions of the most stable isomers of the completely saturated Si−B−H−Cl species. Several trends in the reaction enthalpies can be observed. (1) Simple fissions of B−Cl, Si−Cl, and B−H bonds tend to be the most endothermic decomposition reactions, with $\Delta H°_{rxn}(298) \geq 100$ kcal mol^{-1}. Si−H bond fissions tend to be lower, in the range of 70−85 kcal mol^{-1}. For these bond fissions, reactions with bridge-bonded products are more endothermic than reactions with "normal" products. (2) Straight Si−B bond fission reactions have endothermicities in the 75−90 kcal mol^{-1} range. Breaking the Si−B bond by shifting a H and eliminating a silylene is considerably easier, with endothermicities in the 40−55 kcal mol^{-1} range. (3) H_2 and HCl elimination reactions have endothermicities comparable to silylene elimination reactions and thus are also favored decomposition pathways. HCl elimination reactions are generally more endothermic than H_2 elimination reactions. The 1,1 eliminations from the B tend to be less favored than 1,2 eliminations from the Si and B, which in turn tend to be less favored than 1,1 elimination reactions from the Si. In all of these cases, reactions with bridged or cyclic products tend to be less endothermic than those with "normal" products. (4) Isomerizations have low endothermicities and may thus occur with relative ease. We did find a substantial kinetic barrier for the concerted isomerization $H_2ClSiBH_2 \rightarrow ClSi(H_2)BH_2$. This suggests that such isomerizations are likely to occur in a stepwise fashion via singly bridged geometries, which were found to be unstable at our levels of theory.

We examine silylborane decomposition reactions in more detail as a model for reactions of Si−B−H−Cl compounds. The most likely decomposition reactions are the silylene and H_2 eliminations with $\Delta H°_{rxn}$ of 51.6 and 49.0 kcal mol^{-1}, respectively. There are reactions with lower endothermicities, but they involve formation of bridged and dibridged species. The extent of molecular rearrangement involved in these reactions makes it highly unlikely that they occur in a single step without an activation barrier in addition to the endothermicity.

TABLE 6: Calculated Bond Dissociation Enthalpies (BDEs) at 298 K (kcal mol^{-1})[a]

bond	BDE	bond	BDE	bond	BDE	bond	BDE
(a) Si−H Bonds							
$H-SiH_3$	91.3	$H-SiH_2$	69.5	$H-SiH$	78.3	$H-Si$	68.5
$H-SiH_2BH_2$	78.7	$H-SiHBH_2$	74.5	$H-SiBH_2$	71.1		
$H-SiH_2BH$	60.6	$H-SiHBH$	74.3	$H-SiBH$	60.2		
$H-SiH_2B$	77.9	$H-SiHB$	67.0	$H-SiB$	80.7		
$H-Si(H_2)BH_2$	74.7	$H-Si(H)BH_2$	56.6				
$H-Si(H_2)BH$	22.0						
$H-SiH_2BHSiH_3$	76.6	$H-SiHBHSiH_3$	74.1				
$H-SiH_2BHSiH$	85.4	$H-SiHBHSiH$	65.8				
$H-SiH(BH_2)_2$	73.1	$H-Si(BH_2)_2$	66.3				
$H-SiH_2BHCl$	83.5	$H-SiHBHCl$	72.5	$H-SiBHCl$	73.1		
$H-SiH_2BCl$	57.8	$H-SiHBCl$	75.2	$H-SiBCl$	62.8		
$H-SiHClBH_2$	81.6	$H-SiClBH_2$	68.1				
$H-SiHClBH$	64.4	$H-SiClBH$	75.9				
$H-Si(H_2)BHCl$	75.3						
(b) H Bridge Bonds							
$H_{br}-SiH(H)BH_2$*	78.7	$H_{br}-Si(H)BH_2$*	60.6			$H_{br}-Si(H_2)B$*	51.4
		$H_{br}-SiHBH_2$*	62.5	$H_{br}-SiBH_2$*	77.0		
$H_{br}-SiH(H)BHCl$*	79.5	$H_{br}-SiHBHCl$*	55.4				
$H_{br}-SiCl(H)BH_2$*	79.2	$H_{br}-SiClBH_2$*	63.4				
(c) Si−Cl Bonds							
$Cl-SiH_3$	108.4	$Cl-SiH_2$	85.9	$Cl-SiH$	104.2	$Cl-Si$	68.6
$Cl-SiH_2BH_2$	96.1	$Cl-SiHBH_2$	89.0	$Cl-SiBH_2$	92.0		
$Cl-SiH_2BH$	78.6	$Cl-SiHBH$	88.5	$Cl-SiBH$	72.8		
		$Cl-SiHB$	80.9	$Cl-SiB$	97.6		
$Cl-Si(H_2)BH_2$	97.0	$Cl-Si(H)BH_2$	78.4				
$Cl-Si(H_2)BH$	45.9						
$Cl-Si(H_2)B$	60.0			$Cl-SiBCl$	74.7		
(d) B−H Bonds							
$H-BH_2$	105.3	$H-BH$	78.9	$H-B$	84.6		
$H-BHSiH_3$	101.4	$H-BHSiH_2$	83.3	$H-BHSiH$	83.1	$H-BHSi$	72.2
$H-BSiH_3$	86.7	$H-BSiH_2$	104.0	$H-BSiH$	96.7	$H-BSi$	117.2
$H-BH(H_2)SiH$	103.8	$H-BH(H_2)Si$	51.1				
		$H-B(H_2)Si$	102.9				
$H-B(SiH_3)_2$	97.4	$H-B(SiH_2)(SiH_3)$	79.4			$H-B(SiH)(SiH_2)$	61.7
$H-BHSiH_2BH_2$	101.6						
$H-BClSiH_3$	100.1	$H-BClSiH_2$	74.4	$H-BClSiH$	77.1	$H-BClSi$	66.8
		$H-BCl(H_2)Si$	51.6				
$H-BHSiH_2Cl$	100.8	$H-BHSiHCl$	83.6	$H-BHSiCl$	91.4		
		$H-BSiHCl$	104.3	$H-BSiCl$	92.4		
$H-BH(H_2)SiCl$	102.2						
$H-B(H_2)SiCl$	88.8						
(e) B−Cl Bonds							
$Cl-BH_2$	124.9	$Cl-BH$	99.2	$Cl-B$	120.2	$Cl-BCl_2$	118.2
$Cl-BHSiH_3$	120.5	$Cl-BHSiH_2$	97.6	$Cl-BHSiH$	99.4	$Cl-BHSi$	86.5
$Cl-BSiH_3$	107.1	$Cl-BSiH_2$	127.2	$Cl-BSiH$	119.0	$Cl-BSi$	136.9
$Cl-BH(H_2)Si$	60.5	$Cl-B(H_2)Si$	111.8				
				$Cl-BSiCl$	114.0	$Cl-BClSi$	83.3
(f) Si−B Bonds							
H_3Si-BH_2	87.4	H_2Si-BH_2	78.2	$HSi-BH_2$	82.0	$Si-BH_2$	79.4
H_3Si-BH	64.9	H_2Si-BH	73.8	$HSi-BH$	77.8	$Si-BH$	86.1
H_3Si-B	62.8	H_2Si-B	54.4	$HSi-B$	65.7	$Si-B$	53.5
$H_3Si-BHSiH_3$	84.9	$H_2Si-BHSiH_3$	77.8	$HSi-BHSiH_3$	82.0		
$H_3Si-BHSiH_2$	68.9			$HSi-BHSiH_2$	57.2		
$H_3Si-BHSiH$	69.1	$H_2Si-BHSiH$	53.2	$HSi-BHSiH$	43.5		
$H_3Si-BSiH_3$	74.2	$H_2Si-BSiH_3$	85.1				
$H_3Si-BSiH_2$	93.5			$HSi-BSiH_2$	99.5		
$H_3Si-B(H_2)Si$	91.5	$H_2Si-B(H_2)Si$	73.1	$HSi-B(H_2)Si$	83.4		
				$HSi-BH(H_2)Si$	21.9		
$H_3SiSiH_2-BH_2$	86.2	$H_3SiSiH-BH$	80.0				
$H_2B-SiH_2BH_2$	76.2	$H_2B-SiHBH_2$	77.6	$H_2B-SiBH_2$	82.4		
H_2B-SiH_2BH	57.9	$HB-SiH_2BH_2$	53.5				
$H_3Si-BHCl$	86.2	$H_2Si-BHCl$	72.2	$HSi-BHCl$	78.0	$Si-BHCl$	73.4
$H_3Si-BCl$	49.7	$H_2Si-BCl$	61.4	$HSi-BCl$	64.5	$Si-BCl$	70.2
$H_2ClSi-BH_2$	88.4	$HClSi-BH_2$	66.8	$ClSi-BH_2$	72.8		
$H_2ClSi-BH$	66.5	$HClSi-BH$	62.1	$ClSi-BH$	60.3		
		$HClSi-B$	42.4	$ClSi-B$	52.5		
				$ClSi-BCl$	46.3	$Si-BCl_2$	73.3

[a] *H_{br} indicates a H atom bridge bonded between the Si and the B. Thus, $H_{br}-SiH(H)BH_2$ indicates the $HSi(H_2)BH_2 \rightarrow HSi(H)BH_2 + H$ reaction.

Several transition states relevant to silylborane decomposition are included in Table 4. For both the $H_3SiBH_2 \rightarrow SiH_2 + BH_3$ and the $H_3SiBH_2 \rightarrow HSiBH_2 + H_2$ reactions, we found that the transition states have lower enthalpies than the products; i.e., there are no barriers to these reactions other than the endothermicities. Attempts to find a transition state for the H_3SiBH_2

TABLE 7: Calculated Reaction Enthalpies (kcal mol^{-1})

reaction	$\Delta H°_{rxn}(298)$	reaction	$\Delta H°_{rxn}(298)$
$H_3SiBH_2 \rightarrow H_3SiBH + H$	101.4	$H_3SiSiH_2BH_2 \rightarrow H_3SiSiHBH + H_2$	52.5
$\rightarrow HSi(H)BH_2 + H$	90.7	$\rightarrow H_3SiSiBH_2 + H_2$	45.2
$\rightarrow SiH_3 + BH_2$	87.4	$\rightarrow -H_2SiBHSiH_2-$ (cyc) $+ H_2$	34.6
$\rightarrow Si(H_2)BH_2 + H$	86.7	$H_3SiBHCl \rightarrow H_3SiBH + Cl$	120.5
$\rightarrow H_3SiB + H_2$	83.9	$\rightarrow H_3SiB + HCl$	104.1
$\rightarrow H_2SiBH_2 + H$	78.7	$\rightarrow HSi(H)BHCl + H$	100.6
$\rightarrow H_2SiBH + H_2$	57.8	$\rightarrow H_3SiBCl + H$	100.1
$\rightarrow SiH_2 + BH_3$	51.6	$\rightarrow Si(H_2)BHCl + H$	96.4
$\rightarrow HSiBH_2 + H_2$	49.0	$\rightarrow SiH_3 + BHCl$	87.2
$\rightarrow Si(H)BH_2 + H_2$	43.1	$\rightarrow H_2SiBHCl + H$	83.5
$\rightarrow Si(H_2)BH + H_2$	33.6	$\rightarrow H_2SiBH + HCl$	78.0
$\rightarrow HSi(H_2)BH_2$	12.0	$\rightarrow HSiBHCl + H_2$	51.8
$H_2Si(BH_2)_2 \rightarrow HBSiH_2BH_2 + H$	101.6	$\rightarrow SiH_2 + BH_2Cl$	51.1
$\rightarrow Si(H_2)BH_2 + BH_2$	84.2	$\rightarrow Si(H_2)BCl + H_2$	43.8
$\rightarrow H_2SiBH_2 + BH_2$	76.2	$\rightarrow HSi(HCl)BH_2$	23.0
$\rightarrow HSi(BH_2)_2 + H$	73.1	$\rightarrow HSi(H_2)BHCl$	21.1
$\rightarrow HSiBH_2 + BH_3$	45.4	$H_2ClSiBH_2 \rightarrow HSi(H)BH_2 + Cl$	108.1
$\rightarrow Si(H)BH_2 + BH_3$	39.5	$\rightarrow Si(H_2)BH_2 + Cl$	104.1
$\rightarrow Si(BH_2)_2 + H_2$	35.2	$\rightarrow H_2ClSiBH + H$	100.8
$\rightarrow -H_2SiBHBH-$ (cyc) $+ H_2$	24.9	$\rightarrow H_2SiBH_2 + Cl$	96.1
$HB(SiH_3)_2 \rightarrow H_3SiBSiH_3 + H$	97.4	$\rightarrow SiH_2Cl + BH_2$	88.4
$\rightarrow SiH_3 + H_3SiBH$	84.9	$\rightarrow ClSi(H)BH_2 + H$	86.3
$\rightarrow H_2SiBHSiH_3 + H$	76.6	$\rightarrow ClSi(H)BH_2 + H$	86.3
$\rightarrow H_3SiBH_2 + SiH_2$	53.0	$\rightarrow HClSiBH_2 + H$	81.6
$\rightarrow H_2SiBSiH_3 + H_2$	51.8	$\rightarrow H_2SiBH + HCl$	76.3
$\rightarrow HSiBHSiH_3 + H_2$	46.5	$\rightarrow HSiBH_2 + HCl$	67.5
$\rightarrow Si(H)BHSiH_3 + H_2$	35.7	$\rightarrow Si(H)BH_2 + HCl$	61.6
$\rightarrow -H_2SiBHSiH_2-$ (cyc) $+ H_2$	32.0	$\rightarrow Si(H_2)BH + HCl$	52.1
$\rightarrow Si(H_2)BSiH_3 + H_2$	28.5	$\rightarrow SiH_2 + BH_2Cl$	49.4
$H_3SiSiH_2BH_2 \rightarrow H_3SiSiH_2 + BH_2$	86.2	$\rightarrow ClSiBH_2 + H_2$	45.5
$\rightarrow SiH_3 + H_2SiBH_2$	64.8	$\rightarrow SiHCl + BH_3$	43.1
$\rightarrow SiH_2 + H_3SiBH_2$	55.6	$\rightarrow HSi(HCl)BH_2$	21.3
$\rightarrow HSiSiH_3 + BH_3$	52.5	$\rightarrow ClSi(H_2)BH_2$	7.1

$\rightarrow H_2SiBH + H_2$ reaction were not successful, but the calculations suggested that there should be a high barrier. Attempts to find a transition state for the $H_3SiBH_2 \rightarrow H_3SiB + H_2$ reaction were also unsuccessful, but the calculations suggested that the reaction proceeds directly. We did determine transition states for the isomerization of $HSiBH_2$ to the bridged species and found no activation barriers. Thus, a picture emerges in which H_3SiBH_2 decomposes via both silylene elimination and 1,1 H_2 elimination from the Si to form $HSiBH_2$, with the activation energies determined by the endothermicities. $HSiBH_2$ then isomerizes to $Si(H)BH_2$, and then to $Si(H_2)BH$ in barrierless, exothermic reactions. It is reasonable to expect a similar set of elimination and isomerization reactions to occur with the larger and/or substituted molecules.

The decomposition of silylborane can be compared with the decomposition of disilane. Our calculations for disilane[13,14] indicated that the silylene elimination and 1,1 H_2 elimination reactions are endothermic by 53.9 and 55.8 kcal mol^{-1}, respectively, with no additional activation barriers. In contrast, the 1,2 H_2 elimination reaction, $Si_2H_6 \rightarrow H_2Si{=}SiH_2 + H_2$, is endothermic by 43.8 kcal mol^{-1} but has an additional activation barrier of ~45 kcal mol^{-1}. Comparing these numbers to the values in Table 7 indicates that having a BH_2 group instead of the SiH_3 group reduces the enthalpy required for the SiH_2 and 1,1 H_2 elimination reactions by 2.3 and 6.8 kcal mol^{-1}, respectively. This leads to the H_2 elimination reaction being energetically favored rather than the SiH_2 elimination reaction. The presence of the BH_2 rather than the SiH_3 group also increases the endothermicity for the 1,2 H_2 elimination by 14 kcal mol^{-1}.

Other reactions listed in Table 7 show the effects of additional substitutions. For silylene elimination reactions, putting an additional BH_2 group on the silicon further reduces the energy requirements. The endothermicity for the $H_2Si(BH_2)_2 \rightarrow HSiBH_2 + BH_3$ reaction is only 45.4 kcal mol^{-1}, ~6 kcal mol^{-1} lower than for H_3SiBH_2. However, it appears that putting an additional silyl group on silylborane counteracts the effect of the initial BH_2 substitution. The endothermicities for the $HB(SiH_3)_2 \rightarrow H_3SiBH_2 + SiH_2$ and $H_3SiSiH_2BH_2 \rightarrow SiH_2 + H_3SiBH_2$ reactions of 53.0 and 55.6 kcal mol^{-1} are more like the $Si_2H_6 \rightarrow SiH_2 + SiH_4$ value of 53.9 kcal mol^{-1} than the $H_3SiBH_2 \rightarrow SiH_2 + BH_3$ value of 51.6 kcal mol^{-1}. For reactions involving the 1,1 elimination of H_2 from Si, the presence of an additional BH_2 group continues to reduce the energy requirements. $\Delta H°_{rxn}$ for the $H_2Si(BH_2)_2 \rightarrow Si(BH_2)_2 + H_2$ reaction is only 35.2 kcal mol^{-1}. In this case, however, the presence of a second silyl group also results in a reduction. The endothermicities for the $HB(SiH_3)_2 \rightarrow HSiBHSiH_3 + H_2$ and $H_3SiSiH_2BH_2 \rightarrow H_3SiSiBH_2 + H_2$ reactions are 46.5 and 45.2 kcal mol^{-1}, respectively, somewhat less than the 49.0 kcal mol^{-1} for H_3SiBH_2.

For $HB(SiH_3)_2$ and $H_3SiSiH_2BH_2$, there are also low endothermicity decomposition reactions that produce $-H_2SiBHSiH_2-$ (cyc) and hydrogen. As in the case of the reactions with bridged products, these reactions probably also occur in two steps, with the 1,1 elimination of H_2 followed by insertion of the silylene produced into a Si−H or B−H bond on the other end of the molecule. Such silylene insertions are often barrierless processes, so we expect the rate limitation to be provided by the endothermicity of the initial H_2 elimination of 45−47 kcal mol^{-1}. We note that in silylborane the energy required for silylene elimination was only slightly higher than that for H_2 elimination but that increasing the overall size of the molecule preferentially reduces the energy required for the H_2 elimination reactions.

Decomposition reactions of the chlorinated silylborane involve the same basic chemistry, although the presence of the chlorine increases the number of possible decomposition reactions and alters the energetics somewhat. For $H_2ClSiBH_2$ and $H_3SiBHCl$, as for H_3SiBH_2, the least endothermic reactions (other than isomerizations) are silylene elimination (SiH_2 or HSiCl) and the 1,1 elimination of H_2 from the silicon. Chlorine substitution on the B has little effect on the energetics of these reactions. ΔH°_{rxn} is 51.1 kcal mol^{-1} for $H_3SiBHCl \rightarrow SiH_2 + BH_2Cl$, which is basically the same as the 51.6 kcal mol^{-1} for $H_3SiBH_2 \rightarrow SiH_2 + BH_3$. For the H_2 elimination reaction, Cl substitution on the B raises the endothermicity slightly from 49.0 to 51.1 kcal mol^{-1}. In contrast, Cl substitution on Si reduces the endothermicity of the silylene elimination reaction significantly from 51.6 to 43.1 kcal mol^{-1}, while lowering the endothermicity of the H_2 elimination reaction from 49.0 to 45.5 kcal mol^{-1}. The transition states included in Table 4 for chlorinated species indicate that the SiH_2 and HSiCl elimination reactions have no barriers to reaction other than the endothermicity. This should also be true for the H_2 elimination reaction, based on our results for H_3SiBH_2.

For $H_2ClSiBH_2$, reactions involving HCl elimination from the Si come next in order of increasing endothermicity. In analogy with the 1,1 elimination of H_2 from H_3SiBH_2, we expect the 1,1 elimination of HCl also to occur sequentially with the initial elimination step producing $HSiBH_2$, followed by isomerization to the bridged species. Unlike H_3SiBH_2, however, the $H_2ClSiBH_2 \rightarrow HSiBH_2 + HCl$ reaction appears to have a small activation barrier in addition to the endothermicity. The transition state is 70.6 kcal mol^{-1} above the reactant or 3.1 kcal mol^{-1} greater than ΔH°_{rxn}. We also found a different transition state for 1,1 HCl elimination that is another 3.1 kcal mol^{-1} higher in energy. This has a significantly different geometry in which the departing H atom interacts with the Cl, Si, and B, so we write it as $[HClSi(H)BH_2] \rightarrow HSiBH_2 + HCl$, where the square brackets indicate that the singly bridged species is not stable.

The HCl elimination from $H_2ClSiBH_2$ can be compared with the analogous reaction in a chlorinated disilane. Applying our calculational methods to the 1,1 elimination of HCl from H_3SiSiH_2Cl[47] results in an activation energy that is virtually the same as the endothermicity of 73.6 kcal mol^{-1}. Thus, it appears that the presence of a BH_2 group instead of the SiH_3 group reduces the endothermicity of the reaction by 6.1 kcal mol^{-1} but reduces the activation energy by only half this amount. Our error estimates for the transition-state enthalpies, however, are comparable to these differences, so such comparisons should be viewed with caution.

Chlorination allowed the adducts $H_2Si{:}BH_2Cl$ and $HClSi{:}BH_3$ to be stable at our level of theory although the fully hydrogenated analogue was not. In $H_2Si{:}BH_2Cl$, the Si−B distance is 4.067 Å while the Si−Cl distance is 3.108 Å. Thus, the attractive interaction lies between the empty p orbitals on the Si and the electron density on the Cl, rather than the between the Si and the B. Likewise, in $HClSi{:}BH_3$, the interaction appears to be between the empty orbitals on the B and the electron density on the Cl. These adducts are weakly bound ($\leq$1 kcal mol^{-1}) and are unlikely to affect the kinetics significantly.

Earlier, we observed that SiH_3-for-H substitutions had only minor effects on BDEs for bonds that were somewhat distant from the center of the substitution. This suggests that increasing the size of the molecule to a cluster or surface may not make major alterations to bond dissociation and/or reaction enthalpies for normal, unstrained configurations. It is thus reasonable to suggest that the following could apply to the surface reactions that occur during the deposition of in situ doped silicon, based on the reaction enthalpy results for gas-phase Si−B−H−Cl molecules. (1) Simple bond scissions of surface Si−H, Si−Cl, B−H, and B−Cl bonds are too endothermic to be important, given the 500−700 °C temperatures used in CVD processes. (2) For hydrides, the presence of boron makes it significantly easier to eliminate H_2 from an adjacent Si atom. In the silicon hydrides, the energy required for silylene elimination is comparable to or slightly lower than that required for H_2 elimination. The presence of the B lowers the energy requirement in both cases, but favors the latter. For conditions under which the elimination of hydrogen from the surface is rate limiting, this would explain an increased deposition rate. (3) For chlorides, information on bond enthalpies as well as temperature-programmed desorption experiments[48] indicates that removing Cl from the surface is much harder than removing H and is believed to be rate limiting in chlorosilane CVD. The presence of B only slightly reduces the energy required for HCl elimination from an adjacent Si. However, having a B and a Cl bonded to Si reduces the energy required for either H_2 elimination or silylene formation. Silylene formation involving the production of gas-phase BH_2Cl provides an additional path for removing chlorine from the surface. This would be consistent with the reduced B dopant incorporation that has been reported for chlorosilane CVD.[8]

The chemical bonding in some of these gas-phase Si−B−H−Cl molecules may also provide some insights into surface chemistry. The presence of stable geometries with bridge-bonded H atoms in gas-phase molecules suggests that similar bridge bonds could occur between surface atoms, either as stable geometries or as transients (transition states). A bridge-bonded H atom could provide a pathway for H migration either between surface Si atoms or between surface Si and B atoms. The pseudocyclic species $-H_2SiBHSiH_2-$ has a Si−Si bond length of 2.64 Å, which is longer than either a bulk Si−Si bond (2.352 Å)[49] or the Si−Si dimer bond distance for the clean (100) surface (∼2.3 Å).[9,10] The stability of this gas-phase species suggests that a BH group on a Si−Si dimer on a (100) surface is likely to prefer a bridged position rather than being bonded to only one of the Si atoms, as this would allow the boron to be trivalent, while allowing the Si−Si bond to stretch and relax somewhat.

IV. Summary

We have obtained a self-consistent set of thermochemical parameters for about 100 molecules in the Si−B−H−Cl system from a combination of ab initio electronic structure calculations and empirically based corrections. The species are silylboranes and chlorosilylboranes, their decomposition fragments, plus a few transition states. In addition to thermochemical properties, we obtained molecular geometries, frequencies, moments of inertia, and electronic energies from the electronic structure calculations. Some of these molecules, particularly the less saturated species, have unusual chemical bonding. The most notable features are the presence of H atoms bridge-bonded between the Si and B atoms and the prevalence of cyclic isomers among the larger unsaturated species.

Our calculations indicate that silylborane is likely to decompose via the elimination of H_2 as well as silylene formation. The former probably involves the 1,1 elimination of the H_2 from the Si, followed by isomerization of the $HSiBH_2$ to the bridged $Si(H)BH_2$ species and then to the dibridged $Si(H_2)BH$ species. In comparison with the analogous reaction in disilane, the presence of the B significantly reduces the energy required to remove H_2 from the adjacent Si. Further BH_2-for-H substitution on the Si results in a decrease in the endothermicity of both the silylene formation and H_2 elimination reactions. In contrast, SiH_3-for-H substitution (on either the Si or the B) counteracts the effect of the BH_2 group on the endothermicity of the silylene formation reaction, while resulting in an additional decrease in the endothermicity of the H_2 elimination reaction. Chlorine substitution on the B has little effect on the endothermicity for silylene formation but increases the endothermicity for H_2 elimination slightly. Chlorine substitution on the Si, however, significantly reduces the energy required for both reactions. For the elimination of HCl from $H_2ClSiBH_2$, the presence of B only slightly reduces the energy required, compared to the analogous reaction in $H_2ClSiSiH_3$. These reductions in reaction energies may help explain how the addition of small amounts of B_2H_6 can alter deposition rates in silicon CVD so greatly.

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Appendix

The Supporting Information data are as follows: Table 1S presents atomic coordinates (in angstroms) obtained from the HF/6-31G* geometry optimization calculations for each of the molecular species. Table 2S gives moments of inertia in atomic units (amu bohr^2), while Table 3S lists scaled vibrational frequencies obtained at the same level of theory. Table 4S presents electronic energies resulting from various perturbation theory calculations using the 6-31G** basis set. The projected UHF (PUHF) and projected UMP2 (PUMP2) energies[41] are given for reference, although they are not used in the derivation of the BACs. Table 5S gives results from the G2 calculations for H_3SiBH_2, $H_2Si{=}BH$, and B_2H_4 that were used to determine the Si−B and B−B BACs.

Table 6S gives polynomial coefficients for C_p, H, and S as a function of temperature in the format of an input file as used by the CHEMKIN package of software.[50,51] Fits are provided for many of the species covered in this paper and are defined by

$$\frac{C_p}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

$$\frac{H}{RT} = a_1 + \frac{a_2}{2}T + \frac{a_3}{3}T^2 + \frac{a_4}{4}T^3 + \frac{a_5}{5}T^4 + \frac{a_6}{T}$$

$$\frac{S}{R} = a_1 \ln(T) + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + a_7$$

This information is also available on request from the authors (e-mail pho@sandia.gov or melius@ca.sandia.gov).

Supporting Information Available: Tables as described in the Appendix (52 pages). Ordering information is given on any current masthead page.

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