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Ab Initio Molecular Orbital Study of the Thermochemistry and Reactions of the Chlorinated Disilenes and Their Isomers ($Si_2H_nCl_{4-n}$)

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Structures, vibrational frequencies, and energies for the chlorinated disilenes, their dibridged isomers, and the transition states connecting the chlorinated disilenes to the corresponding silylsilylenes are presented. Geometries and frequencies were obtained at the MP2/6-31G(d,p) level, and energetics were calculated at the G2, G2(MP2), MP4/6-31+G(2df,p), and/or MP2/6-31+G(2df,p) levels of theory, depending on the number of chlorine atoms in the molecule. The silylsilylene isomer with the structure $H_nCl_{3-n}SiSiCl$ was found to be lowest in energy for all of the chlorinated compounds. The dibridged structures are all significantly higher in energy than the silylsilylene and disilene structures. Barriers for isomerization by H transfer and Cl transfer ranged from 5 to 18 kcal/mol and 9 to 23 kcal/mol above the disilene, respectively. Energies along paths for decomposition of the chlorinated disilenes to pairs of silylenes are presented, confirming that the reverse reactions are barrierless. Finally, energetics of various decomposition products of the $Si_2H_nCl_{4-n}$ compounds are considered. It is shown that for the species with two or more chlorines, decomposition to a pair of silylenes should be the dominant reaction path based on the energetics of competing paths. The isomerization barriers are much smaller than decomposition barriers, so the isomerization reactions will be fast compared to decomposition.

Introduction

The chlorinated silanes, particularly dichlorosilane and trichlorosilane, are used as precursors for the chemical vapor deposition (CVD) of epitaxial silicon. At the high temperatures where this process is carried out, homogeneous decomposition of the precursor molecules may play an important role by generating reactive species that lead to film growth. Secondary reactions can both accelerate the decomposition of the precursor and consume reactive intermediates that could otherwise lead to film growth. Production of high concentrations of reactive intermediates can lead to unwanted homogeneous nucleation of particles. Homogeneous unimolecular decomposition of the chlorinated silanes leads to production of silylenes (SiH_2, SiHCl, and $SiCl_2$). These species can insert into the parent silanes to give chlorinated disilanes that then decompose by eliminating a silylene or hydrogen. Hydrogen elimination from the disilanes produces silylsilylenes. These can isomerize to the corresponding disilenes, which can then decompose to a pair of silylenes. This gives rise to chain mechanisms for chlorosilane decomposition such as

$$SiH_2 + SiH_2Cl_2 \leftrightarrow HCl_2SiSiH_3 \tag{1}$$

$$HCl_2SiSiH_3 \leftrightarrow HCl_2SiSiH + H_2 \tag{2}$$

$$HCl_2SiSiH \leftrightarrow Cl_2SiSiH_2 \tag{3}$$

$$Cl_2SiSiH_2 \leftrightarrow SiH_2 + SiCl_2 \tag{4}$$

which is a silylene-catalyzed cycle for the overall decomposition $SiH_2Cl_2 \leftrightarrow SiCl_2 + H_2$. Note that reactions 1−4 comprise a degenerate chain-branching sequence. Of course, at each step in the above set of reactions there are other competing processes. We have previously studied the silylene and hydrogen eliminations such as reactions 1 and 2.[1] In this work we consider the isomerization reactions between the chlorinated silylsilylenes and disilenes and the decomposition of the disilenes to pairs of silylenes. An understanding of the energetics of these reactions is necessary to understand the role of chain processes such as the one described above in decomposition of the chlorinated silanes and chemical vapor deposition of silicon from them.

Disilene, silylsilylene, and the isomerization between them have been considered in numerous theoretical studies,[2−9] but the analogous chlorinated species have been studied relatively little. Allendorf and Melius[10] have calculated heats of formation of $Cl_3SiSiCl$ and $Cl_2SiSiCl_2$ using the BAC-MP4 methodology. Bell et al.[11] calculated energies for all of the chlorinated silylsilylenes and disilenes using the semiempirical MOBI method. To our knowledge the isomerizations between the chlorinated silylsilylenes and disilenes have not previously been studied theoretically or experimentally. Theoretical investigations of the thermochemistry and reactions of the silanes and halosilanes through 1992 were reviewed by Gordon et al.[12] Several studies[13−17] have suggested that, in addition to dimerizing to form disilanes, silylenes can dimerize to form dibridged structures such as the one illustrated in Figure 1b. For Si_2H_4, Trinquier[15] predicted the dibridged structure to be about 22.5 kcal/mol above the disilene. Spoliti et al.[13] presented geometries for the dibridged Si_2Cl_4 species but did not compare their energies to the analogous tetrachlorodisilene. Trinquier et al.[16] found that the dibridged form of Si_2F_4 was a few kilocalories per mole above the silylsilylene form, which was the lowest energy structure.

In this work, we present calculated structures, vibrational frequencies, and energies for the chlorinated disilenes and the dibridged structures with stoichiometry $Si_2H_nCl_{4-n}$. We have

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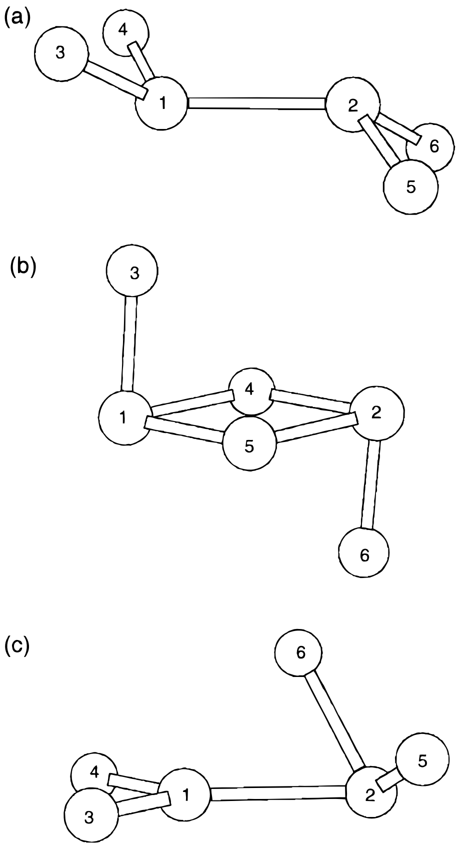

Figure 1. Generic geometries for molecules and transition states. Atoms 1 and 2 are silicon; atoms 3 through 6 are hydrogen or chlorine. Bond lengths and angles are given in Table 2.

presented calculations at the same levels of theory for the silylsilylene structures in our previous work.[1] This gives us a complete picture of the relative stability of the isomers and how it changes with chlorine substitution. We also present calculated structures, vibrational frequencies, and energies for the transition states connecting the chlorinated disilenes to their silylsilylene isomers. Finally, we present energetic profiles for dimerization of the chlorinated silylenes to disilenes. These confirm that the dimerization reactions are barrierless and give an idea of the range of interaction between the chlorinated silylenes as they dimerize.

Computational Methods

The ab initio molecular orbital calculations presented here were carried out using the GAUSSIAN 94 series of programs.[24] Geometries were fully optimized using the "tight" convergence criteria at the MP2(full)/6-31G(d,p) level using analytical gradients. Vibrational frequencies were obtained at this same level using analytical second derivatives. The frequency calculations verified that the points located were indeed minima or first-order saddle points with zero or one imaginary frequency, respectively. Energies were calculated using a larger basis set and second-order Møller–Plesset perturbation theory (MP2/6-31+G(2df,p), frozen core) for all of the species considered. For molecules and transition states with three or fewer chlorine atoms, energies were also calculated using fourth-order Møller–Plesset theory (MP4SDTQ/6-31+G(2df,p),frozen core) and at the G2(MP2)[25] level. Full G2[26] energy calculations were performed for those molecules with two or fewer chlorines. The G2 methods approximate a quadratic configuration interaction[27] calculation at the QCISD(T)/6-311+G(3df,2p) level by applying basis set corrections additively to a QCISD(T)/6-311G(d,p) calculation.[26] In the original G2 method, some of these corrections are calculated at the MP4 level, whereas in the modified G2(MP2) method, all of the corrections are calculated at the MP2 level.[25] In both cases, zero-point energy based on the HF/6-31G(d) frequencies, scaled by 0.8929, is added to the energy, as is an empirical correction based on the number of paired and unpaired electrons in the molecule. Note that in the isomerization reactions considered here all of the electrons remain formally paired, so that this empirical correction in the G2 methods cancels when taking energy differences between a reactant and product or transition state.

Results and Discussion

The total energies for all of the species considered here are presented in Table 1. The G2 energy for disilene has been previously presented by Curtiss et al.[8] and is repeated here only for convenience. The zero-point and thermal energies in Table 1 were calculated from the geometries and unscaled frequencies at the MP2(full)/6-31G(d,p) level in the rigid rotor, harmonic oscillator approximation.

Geometries and Vibrational Frequencies. Generic representations of a disilene, a dibridged isomer, and a disilene-to-silylsilylene transition state are illustrated in Figure 1a,b,c, respectively. In each case, the atoms numbered 1 and 2 are silicon, while those numbered 3 through 6 may be chlorine or hydrogen. Geometric parameters for these structures are given in Table 2. The atom labeling in Table 2 corresponds to the numbering in Figure 1. The geometries are described by a set of bond lengths, bond angles relative to the Si–Si bond, and dihedral angles around the Si–Si bond relative to the atom numbered 3 in the figure.

The disilenes are all found to be nonplanar, becoming more so with increasing chlorine substitution. For the fully chlorinated disilene, $Cl_2SiSiCl_2$, the Si–Si–Cl bond angle and Cl–Si–Cl bond angle are only 111° and 107°, respectively. The Si–Si bond length also increases substantially with chlorine substitution. This contrasts with the chlorinated disilanes and silylsilylenes, whose Si–Si bond length changes very little with chlorine substitution. The Si–Si bond in disilene is 0.22 Å shorter than that in disilane at this level of calculation, while the Si–Si bond length in tetrachlorodisilene is 0.02 Å longer than in hexachlorodisilane. The other bond lengths do not change much with chlorine substitution and are close to bond lengths in the chlorinated silanes and disilanes. The geometric changes upon chlorine substitution are consistent with a decrease in π bonding between the silicon atoms.

Only the trans isomers of the dibridged structures, as presented in Figure 1b, were considered in this study. All of the dibridged structures presented here were found to be energy minima. When both of the bridging atoms are hydrogen, the minimum energy dibridged configuration has the bridging atoms in a plane with the two silicon atoms. However, when both bridging atoms are chlorine, the four-membered ring puckers into a nonplanar configuration. The ring is also planar for HSiHClSiH and ClSiHClSiCl, which both have C_2 symmetry. The ring is slightly nonplanar in ClSiHClSiH, which necessarily has no symmetry. The Si–H and Si–Cl bonds to the bridging atoms are 10–15% longer than ordinary Si–H or Si–Cl bonds.

The typical disilene-to-silylsilylene transition-state geometry is shown in Figure 1c. Atom 6 is being transferred from one silicon center to the other. The H_3SiSiH to H_2SiSiH_2 isomerization transition-state structure is essentially the same as that

TABLE 1: Total Energies[a]

	MP2 6-31G(d,p)	MP2 6-31+G(2df,p)	MP4 6-31+G(2df,p)	G2(MP2)	G2	ZPE	thermal + ZPE
Chlorinated Disilenes							
H_2SiSiH_2	−580.292 55	−580.321 07	−580.372 77	−580.423 46	−580.429 17	20.460	23.213
$HClSiSiH_2$	−1039.373 88	−1039.4 49 85	−1039.519 16	−1039.616 68	−1039.630 11	16.845	20.091
cis-HClSiSiHCl	−1498.454 52	−1498.5 78 40	−1498.665 40	−1498.810 28	−1498.831 25	13.140	16.989
trans-HClSiSiHCl	−1498.454 08	−1498.5 77 69	−1498.664 75	−1498.809 65	−1498.830 63	13.114	17.020
Cl_2SiSiH_2	−1498.459 81	−1498.5 83 87	−1498.670 52	−1498.815 13	−1498.836 32	12.905	16.817
$Cl_2SiSiHCl$	−1957.540 26	−1957.7 12 18	−1957.816 69	−1958.008 92		9.158	13.767
$Cl_2SiSiCl_2$	−2416.627 05	−2416.8 47 40				5.103	10.538
Dibridged Structures							
HSiHHSiH	−580.254 72	−580.285 99	−580.339 67	−580.389 83	−580.395 24	21.284	23.676
ClSiHHSiH	−1039.348 27	−1039.4 28 48	−1039.499 03	−1039.595 89	−1039.608 56	17.633	20.546
HSiClHSiH	−1039.334 66	−1039.4 19 46	−1039.489 65	−1039.586 39	−1039.599 29	16.884	19.954
ClSiHHSiCl	−1498.437 99	−1498.5 66 38	−1498.653 96	−1498.798 32	−1498.818 26	13.708	17.324
ClSiClHSiH	−1498.428 93	−1498.5 62 74	−1498.649 87	−1498.793 96	−1498.814 17	12.909	16.690
HSiClClSiH	−1498.408 62	−1498.5 44 51	−1498.631 80	−1498.774 68	−1498.795 33	12.652	16.563
ClSiClHSiCl	−1957.523 56	−1957.7 06 17	−1957.810 22	−1958.001 79		8.889	13.453
ClSiClClSiH	−1957.506 49	−1957.6 91 87	−1957.796 01	−1957.986 76		8.546	13.338
ClSiClClSiCl	−2416.601 22	−2416.8 34 77				4.171	9.980
Isomerization Transition States							
$H_2SiSiH_2 \leftrightarrow H_3SiSiH$	−580.263 57	−580.295 60	−580.346 77	−580.400 06	−580.405 86	19.426	21.885
$HClSiSiH_2 \leftrightarrow H_2ClSiSiH$[c]	−1039.331 60	−1039.413 62	−1039.482 58	−1039.581 16	−1039.594 80	16.099	19.085
$HClSiSiH_2 \leftrightarrow H_3SiSiCl$	−1039.342 31	−1039.422 22	−1039.491 16	−1039.591 31	−1039.604 76	15.676	18.699
$HClSiSiH_2 \leftrightarrow H_2ClSiSiH$[b]	−1039.357 50	−1039.437 04	−1039.505 36	−1039.604 88	−1039.618 47	15.851	18.818
$Cl_2SiSiH_2 \leftrightarrow H_2ClSiSiCl$	−1498.415 41	−1498.544 82	−1498.631 27	−1498.777 96	−1498.799 23	11.967	15.809
cis-HClSiSiHCl $\leftrightarrow H_2ClSiSiCl$	−1498.435 73	−1498.563 22	−1498.649 37	−1498.796 06	−1498.817 20	12.102	15.696
trans-HClSiSiHCl $\leftrightarrow H_2ClSiSiCl$	−1498.431 56	−1498.560 01	−1498.646 16	−1498.792 83	−1498.813 91	11.887	15.630
trans-HClSiSiHCl $\leftrightarrow HCl_2SiSiH$	−1498.427 62	−1498.557 35	−1498.643 66	−1498.788 32	−1498.809 61	12.643	16.148
cis-HClSiSiHCl $\leftrightarrow HCl_2SiSiH$	−1498.422 83	−1498.552 95	−1498.639 20	−1498.784 36	−1498.805 53	12.295	15.915
$Cl_2SiSiH_2 \leftrightarrow HCl_2SiSiH$	−1498.447 76	−1498.575 93	−1498.661 33	−1498.807 85	−1498.829 08	11.843	15.470
$Cl_2SiSiHCl \leftrightarrow Cl_3SiSiH$	−1957.518 67	−1957.696 05	−1957.799 79	−1957.991 63		8.658	12.887
$Cl_2SiSiHCl \leftrightarrow HCl_2SiSiCl$[b]	−1957.526 23	−1957.702 44	−1957.805 83	−1957.999 45		8.056	12.435
$Cl_2SiSiHCl \leftrightarrow HCl_2SiSiCl$[c]	−1957.511 63	−1957.688 90	−1957.792 87	−1957.985 78		8.517	12.919
$Cl_2SiSiCl_2 \leftrightarrow Cl_3SiSiCl$	−2416.607 79	−2416.831 67				4.370	9.683

[a] Total energies in hartrees (1 hartree = 627.51 kcal/mol), zero-point energies (ZPE) and thermal energy in kcal/mol at 298 K and 1 atm using geometry and unscaled frequencies at the MP2/6-31G(d,p) level. MP2/6-31+G(2df,p) and MP4/6-31+G(2df,p) energies are at MP2/6-31G(d,p) geometry. Note that G2 and G2(MP2) energies include zero-point energy calculated using scaled HF/6-31G(d) frequencies. Entries left blank were not calculated because of computational expense. [b] Transition state corresponding to H atom transfer. [c] Transition state corresponding to Cl atom transfer.

reported in previous studies,[2,4,5] with only slight changes due to differing types and levels of calculation. The good agreement with the calculations of Ernst et al.,[2] who used complete active space multiconfigurational self-consistent-field (CAS(6,6)) wave functions for the geometry optimizations, provides an indication that our single-reference-based approach works well for these reactions. At the MP2/6-31G(d,p) level, the energy at their geometry is only 0.4 kcal/mol above that at the geometry given here. The geometries of the transition states for chlorine atom transfer are very similar to those for H atom transfer. In both cases, the atom being transferred remains much closer to the silicon atom that it is bound to in the disilene. This bond is typically lengthened by about 5% of its value in the disilene for H transfer and about 8% for Cl transfer. By contrast, the distance to the other silicon is typically 40−50% longer than the corresponding equilibrium bond length. The Si−Si bond in these transition states is longer than in the disilene isomer, but shorter than in the silylsilylene isomer and is slightly longer for Cl atom transfer than for H atom transfer.

The transition-state geometry for the fully chlorinated species ($Cl_2SiSiCl_2 \leftrightarrow Cl_3SiSiCl$) is somewhat different from the other transition states. The Si−Si distance is 0.22 Å longer than for the Cl transfer $Cl_2SiSiHCl \leftrightarrow HCl_2SiSiCl$. The Si−Cl bond to the atom being transferred is less extended than in the other structures. The dihedral angles about the Si−Si bond are also different than in the other transition states. Reoptimizing this structure and following the intrinsic reaction coordinate (IRC)[22,23] at the HF/6-31G(d) level showed that at that level this transition state connects the silylsilylene to a pair of separated dichlorosilylene molecules rather than to tetrachlorodisilane. However, reoptimizing the structure and following the intrinsic reaction coordinate using density functional theory with the B3LYP functional[24] showed that at that level the path through this saddle point connects the silylsilylene and disilene structures. Likewise, following the intrinsic reaction coordinate at the MP2/6-31G(d,p) level showed that this saddle point connects the silylsilylene and disilene structures. At the MP2/6-31G(d,p) level we also located another saddle point of similar geometry whose imaginary frequency corresponded to a torsional motion about the Si−Si bond. The results of these geometry optimizations and reaction path following, as well as the calculated vibrational frequencies presented in Table 3, indicate that the potential surface is quite flat near this saddle point.

Unscaled vibrational frequencies calculated at the MP2/6-31G(d,p) level are presented in Table 3. There are no experimental frequencies with which to compare these calculated results, but previous studies on the chlorinated silanes and disilanes[1,25] suggest that a scaling factor near 0.95 would be appropriate to match them to experimental anharmonic frequencies. For the disilenes, the lowest frequency motion corresponds to a bending motion of the Si−Si bond (what would be the in-plane bending motion, if the molecules were planar), except for $Cl_2SiSiCl_2$, where the lowest frequency corresponds to a

TABLE 2: Parameters of MP2/6-31G(d,p) Optimized Geometries[a]

chlorinated disilenes (Figure 1a)	atom labels	symmetry	R(1-2)	R(1-3)	R(1-4)	R(2-5)	R(2-6)	∠213	∠214	∠125	∠126	∠4123	∠5213	∠6213
H_2SiSiH_2	SiSiH H H H	C_{2h}	2.164	1.471	1.471	1.471	1.471	118.8	118.8	118.8	118.8	143.6	36.4	180.0
$HClSiSiH_2$	SiSiH H H Cl	C_1	2.188	1.476	1.474	1.473	2.053	110.6	114.8	120.0	120.7	127.9	49.8	−170.8
cis-HClSiSiHCl	SiSiH ClH Cl	C_2	2.220	1.478	2.054	1.478	2.054	111.6	118.8	111.6	118.8	126.8	62.9	−170.3
trans-HClSiSiHCl	SiSiClH H Cl	C_1	2.221	2.060	1.476	1.476	2.060	114.8	115.9	115.9	114.8	127.1	52.9	180.0
Cl_2SiSiH_2	SiSiH H ClCl	C_s	2.218	1.481	1.481	2.044	2.044	105.4	105.4	120.5	120.5	115.3	52.3	−167.6
$Cl_2SiSiHCl$	SiSiH ClClCl	C_1	2.267	1.483	2.064	2.051	2.045	105.9	112.4	114.0	118.3	116.0	64.2	−166.9
$Cl_2SiSiCl_2$	SiClClClClCl	C_{2h}	2.343	2.056	2.056	2.056	2.056	111.0	111.0	111.0	111.0	119.0	61.0	180.0

dibridged structures (Figure 1b)	atom labels	symmetry	R(1-2)	R(1-3)	R(1-4)	R(1-5)	R(2-4)	R(2-5)	R(2-6)	∠213	∠214	∠215	∠126	∠4123	∠5213	∠6213
HSiHHSiH	SiSiH H H H	C_{2h}	2.572	1.504	1.643	1.643	1.643	1.643	1.504	87.6	38.5	38.5	87.6	90.0	90.0	180.0
ClSiHHSiH	SiSiH H H Cl	C_s	2.577	1.507	1.615	1.615	1.683	1.683	2.096	78.5	39.6	39.6	100.5	98.9	98.9	180.0
HSiClHSiH	SiSiH H ClH	C_2	2.827	1.503	1.655	2.280	1.655	2.280	1.503	88.1	31.3	51.7	88.1	87.5	92.5	−175.0
ClSiHHSiCl	SiSiClH H Cl	C_{2h}	2.636	2.095	1.658	1.658	1.658	1.658	2.095	94.0	37.3	37.3	94.0	90.0	90.0	180.0
ClSiClHSiH	SiSiH H ClCl	C_1	2.862	1.505	1.631	2.289	1.696	2.294	2.090	84.5	31.3	51.4	99.8	94.8	95.3	−171.6
HSiClClSiH	SiSiH ClClH	C_s	3.247	1.503	2.329	2.329	2.336	2.336	1.500	68.2	46.0	46.0	111.1	110.8	110.8	180.0
ClSiHClSiCl	SiSiClH ClCl	C_2	2.920	2.089	1.672	2.306	1.672	2.306	2.089	96.7	29.2	50.7	96.7	84.8	95.2	−169.7
ClSiClClSiH	SiSiH ClClCl	C_s	3.241	1.505	2.323	2.323	2.373	2.373	2.074	65.0	47.0	47.0	122.9	113.5	113.5	180.0

isomerization transition states (Figure 1c)	atom labels	symmetry	R(1-2)	R(1-3)	R(1-4)	R(2-5)	R(2-6)	R(1-6)	∠213	∠214	∠125	∠126	∠4123	∠5213	∠6213
$H_2SiSiH_2 \leftrightarrow H_3SiSiH$	SiSiH H H H	C_1	2.214	1.485	1.478	1.501	1.548	2.134	134.8	119.5	89.6	66.4	178.0	−21.3	−120.7
$HClSiSiH_2 \leftrightarrow H_2ClSiSiH$[c]	SiSiH H H Cl	C_1	2.291	1.486	1.474	1.507	2.221	2.878	133.1	121.6	87.2	79.3	−178.6	−29.0	−126.2
$HClSiSiH_2 \leftrightarrow H_3SiSiCl$	SiSiH H ClH	C_1	2.242	1.486	1.479	2.109	1.559	2.166	141.5	111.2	105.6	66.7	−173.6	−18.1	−117.8
$HClSiSiH_2 \leftrightarrow H_2ClSiSiH$[b]	SiSiH ClH H	C_1	2.221	1.482	2.048	1.516	1.540	2.187	132.0	124.9	78.2	68.4	175.3	−21.0	−118.8
$Cl_2SiSiH_2 \leftrightarrow H_2ClSiSiCl$	SiSiH H ClCl	C_1	2.368	1.487	1.478	2.120	2.197	2.991	137.5	116.8	99.8	81.8	−168.7	−20.9	−122.3
cis-HClSiSiHCl ↔ $H_2ClSiSiCl$	SiSiClH ClH	C_1	2.245	2.046	1.480	2.095	1.563	2.120	143.5	110.1	108.6	64.8	−170.6	−23.5	−121.3
trans-HClSiSiHCl ↔ $H_2ClSiSiCl$	SiSiH ClClH	C_1	2.281	1.484	2.039	2.133	1.548	2.266	135.2	119.8	96.1	69.6	−178.0	−10.0	−108.9
trans-HClSiSiHCl ↔ HCl_2SiSiH	SiSiClH H Cl	C_1	2.299	2.041	1.475	1.505	2.218	2.844	132.7	123.0	88.3	78.0	−176.6	−32.6	−130.1
cis-HClSiSiHCl ↔ HCl_2SiSiH	SiSiH ClH Cl	C_1	2.322	1.484	2.028	1.518	2.207	2.941	131.6	125.3	79.4	80.9	176.3	−18.8	−115.7
$Cl_2SiSiH_2 \leftrightarrow HCl_2SiSiH$	SiSiClClH H	C_1	2.235	2.045	2.042	1.508	1.549	2.137	132.1	122.2	83.3	65.9	176.3	−18.5	−114.6
$Cl_2SiSiHCl \leftrightarrow Cl_3SiSiH$	SiSiClClH Cl	C_1	2.362	2.037	2.027	1.510	2.201	2.948	130.8	122.6	83.5	80.4	176.5	−14.0	−111.0
$Cl_2SiSiHCl \leftrightarrow HCl_2SiSiCl$[b]	SiSiClClClH	C_1	2.306	2.036	2.038	2.116	1.554	2.217	134.7	117.4	99.1	66.9	179.9	−9.7	−107.0
$Cl_2SiSiHCl \leftrightarrow HCl_2SiSiCl$[c]	SiSiClH ClCl	C_1	2.392	2.035	1.481	2.108	2.193	2.963	137.1	117.8	100.8	80.4	−168.9	−23.6	−125.1
$Cl_2SiSiCl_2 \leftrightarrow Cl_3SiSiCl$	SiSiClClClCl	C_1	2.616	2.039	2.037	2.113	2.141	3.270	133.9	119.3	94.1	86.3	177.5	3.9	−97.4

[a] Bond lengths in angstroms; bond angles and dihedral angles in degrees. Atom numbering as shown in Figure 1, i.e., SiSiH ClH Cl means the atoms labeled 1 and 2 are Si, atoms 3 and 5 are H, and atoms 4 and 6 are Cl in Figure 1a. [b] Transition state corresponding to H atom transfer. [c] Transition state corresponding to Cl atom transfer.

torsional motion around the Si−Si bond. For the dibridged structures, the lowest frequency motion is bending or puckering of the four-membered ring. In all cases, the imaginary frequency of the saddle point structures corresponded to atom transfer from one silicon atom to the other.

Heats of Formation. Table 4 presents calculated heats of formation for the chlorinated disilenes and dibridged structures studied here. These were calculated using the reaction

$$SiH_2 + Si_2H_6 + (n/4)SiCl_4 \rightarrow Si_2H_{4-n}Cl_n + (1 + n/4)SiH_4$$

and experimentally determined heats of formation of SiH_4,[26] $SiCl_4$,[26] Si_2H_6,[27] and SiH_2.[28] This is the same reaction we previously used to obtain heats of formation for the silylsilylenes.[1] Therefore, the energy differences between these compounds and the silylsilylenes obtained using these heats of formation and our previously presented heats of formation for the silylsilylenes are the same as would be obtained by direct comparison of the energies from the ab initio calculations. For the disilenes, we see that the calculated heats of formation change very little with the level of calculation from the MP2/6-31G(d,p) level to the G2 calculation. For the dibridged structures, the heats of formation calculated at the MP2/6-31G-(d,p) level are several kilocalories per mole higher than those calculated at the higher levels. However, those calculated at the MP2/6-31+G(2df,p) level are in good agreement with the calculations at higher levels.

There are few experimental heats of formation with which to compare the results in Table 4. Ruscic and Berkowitz[29] obtained a heat of formation of 65.7 ± 0.9 kcal/mol for H_2SiSiH_2 from a photoionization mass spectrometric study. Our value of 68.1 kcal/mol is in reasonable agreement, but lies outside their error limits. This may be because we have referenced our value to the heat of formation of disilane (19.1 kcal/mol) from the CATCH tables.[27] The best theoretical results for disilane[8] give a heat of formation of 16.0 kcal/mol. If we had used this value, our heat of formation for H_2SiSiH_2 would be 3.1 kcal/mol lower and in agreement with Ruscic and Berkowitz. There have been many previous theoretical studies of H_2SiSiH_2. Katzer et al.[7] calculated a value of 67.1 kcal/mol using an empirically corrected ab initio scheme based on multiconfiguration wave functions. Curtiss et al.[8] obtained a value of 64.5 kcal/mol based on the enthalpy of atomization at the G2 level. The difference between our result and theirs is due to the reaction and reference compounds we used for calculating the enthalpies. Ho et al.[3] obtained a value of 62.9 kcal/mol using their bond additivity correction method (BAC-MP4). Allendorf and Melius[10] have applied the BAC-MP4 method to $Cl_2SiSiCl_2$ and calculated a heat of formation of −95.7 ± 9.4 kcal/mol. Our value of −94.3 kcal/mol is in good agreement with this. The semiempirical (MOBI) calculations of Bell et al.[11] gave heats of formation that were 15−35 kcal/mol lower than those we present here. This poor agreement is not surprising, since the MOBI method has been shown to be unreliable for silicon compounds.[7]

Isomerization Barriers. Table 5 shows the calculated barriers (electronic plus zero-point energy) for the isomerizations

TABLE 3: Unscaled MP2/6-31G(d,p) Vibrational Frequencies[a]

Chlorinated Disilenes												
H_2SiSiH_2	347	350	471	552	586	636	954	993	2340	2346	2365	2375
$HClSiSiH_2$	136	285	410	440	502	561	630	835	968	2321	2342	2353
cis-HClSiSiHCl	60	159	192	399	423	518	569	631	803	807	2312	2318
trans-HClSiSiHCl	81	101	175	395	416	537	564	623	783	843	2325	2330
Cl_2SiSiH_2	119	166	193	290	389	475	545	625	641	973	2291	2319
$Cl_2SiSiHCl$	59	91	155	160	208	366	489	557	600	627	802	2287
$Cl_2SiSiCl_2$	45	62	121	128	155	197	236	332	518	582	594	602
Dibridged Structures												
HSiHHSiH	313	413	745	886	888	903	1419	1580	1606	1763	2178	2194
ClSiHHSiH	134	351	415	513	604	948	951	1305	1496	1632	1812	2172
HSiClHSiH	176	300	325	396	725	767	805	884	1394	1659	2184	2195
ClSiHHSiCl	81	121	166	439	516	518	835	884	1369	1429	1485	1746
ClSiClHSiH	90	159	262	291	387	494	528	763	922	1316	1640	2179
HSiClClSiH	98	188	198	323	334	358	671	738	766	791	2182	2204
ClSiHClSiCl	60	108	141	178	257	356	381	522	522	858	1334	1500
ClSiClClSiH	77	113	148	157	218	310	332	366	539	751	803	2165
ClSiClClSiCl	35	63	103	125	160	192	213	301	313	342	526	546
Isomerization Transition States												
$H_2SiSiH_2 \leftrightarrow H_3SiSiH$	750i	341	506	546	679	711	974	1051	1978	2196	2279	2328
$HClSiSiH_2 \leftrightarrow H_2ClSiSiH$[c]	368i	249	272	395	443	564	727	780	1050	2147	2280	2354
$HClSiSiH_2 \leftrightarrow H_3SiSiCl$	804i	124	371	416	493	533	677	821	1012	1917	2274	2328
$HClSiSiH_2 \leftrightarrow H_2ClSiSiH$[b]	477i	144	349	422	523	624	633	904	982	1973	2209	2325
$Cl_2SiSiH_2 \leftrightarrow H_2ClSiSiCl$	400i	98	158	232	315	410	431	500	584	1034	2273	2337
cis-HClSiSiHCl $\leftrightarrow H_2ClSiSiCl$	494i	53	202	255	372	516	533	634	826	854	1909	2312
trans-HClSiSiHCl $\leftrightarrow H_2ClSiSiCl$	641i	69	94	175	425	485	582	626	788	827	1958	2284
trans-HClSiSiHCl $\leftrightarrow HCl_2SiSiH$	137i	124	149	309	412	447	597	652	755	891	2164	2343
cis-HClSiSiHCl $\leftrightarrow HCl_2SiSiH$	268i	73	115	313	391	428	597	650	783	871	2096	2282
$Cl_2SiSiH_2 \leftrightarrow HCl_2SiSiH$	374i	130	193	239	318	402	575	621	659	995	1983	2168
$Cl_2SiSiHCl \leftrightarrow Cl_3SiSiH$	94i	66	110	170	206	317	428	582	612	654	771	2142
$Cl_2SiSiHCl \leftrightarrow HCl_2SiSiCl$[b]	348i	57	79	159	203	292	383	497	608	622	798	1937
$Cl_2SiSiHCl \leftrightarrow HCl_2SiSiCl$[c]	154i	46	115	158	189	271	422	470	519	599	858	2309
$Cl_2SiSiCl_2 \leftrightarrow Cl_3SiSiCl$	67i	23	39	64	137	182	215	260	466	497	570	604

[a] Frequencies are in units of cm^{-1} and are unscaled. Degenerate frequencies are simply repeated an appropriate number of times. [b] Transition state corresponding to H atom transfer. [c] Transition state corresponding to Cl atom transfer.

TABLE 4: Calculated Heats of Formation[a]

molecule	MP2 6-31G(d,p)	MP2 6-31+G(2df,p)	MP4 6-31+G(2df,p)	G2(MP2)	G2	S(298)
H_2SiSiH_2	68.2	67.4	68.4	67.2	68.1	64.4
$HClSiSiH_2$	29.5	28.8	29.5	28.3	29.3	73.4
cis-HClSiSiHCl	−8.9	−9.7	−9.3	−10.7	−9.6	81.1
trans-HClSiSiHCl	−8.5	−9.2	−8.8	−10.3	−9.1	81.8
Cl_2SiSiH_2	−12.3	−13.3	−12.6	−13.7	−12.7	81.2
$Cl_2SiSiHCl$	−50.5	−51.5	−51.3	−52.8		89.8
$Cl_2SiSiCl_2$	−92.8	−94.3				96.7
HSiHHSiH	92.4	89.9	89.6	88.0	89.0	62.4
ClSiHHSiH	46.0	42.7	42.6	41.0	42.5	72.1
HSiClHSiH	53.9	47.7	47.9	47.1	48.4	72.3
ClSiHHSiCl	1.9	−1.8	−1.7	−3.5	−1.6	79.8
ClSiClHSiH	6.9	−0.1	0.2	−0.6	1.1	80.4
HSiClClSiH	19.5	11.2	11.4	11.7	13.1	80.7
ClSiClHSiCl	−40.3	−48.1	−47.5	−48.4		88.8
ClSiClClSiH	−29.7	−39.2	−38.7	−38.7		89.5
ClSiClClSiCl	−77.2	−86.9				100.3

[a] Heats of formation in kcal/mol at 298.15 K and 1 atm calculated as described in the text using total energies, thermal, and zero-point energies from Table 1. Entropies are in cal/(mol K) calculated using the unscaled MP2/6-31G(d,p) vibrational frequencies. Reference values for calculating heats of formation were $\Delta H_f(SiH_4) = 8.2$ kcal/mol,[26] $\Delta H_f(SiCl_4) = -158.4$ kcal/mol,[26] $\Delta H_f(SiH_2) = 65.2$ kcal/mol,[28] and $\Delta H_f(Si_2H_6) = 19.1$ kcal/mol.[27] Entries left blank were not calculated because of computational expense.

from the disilenes to the silylsilylenes. Forward and reverse barriers are calculated directly from the electronic and zero-point energies presented in Table 1. Reverse barriers are those from the highest level calculations done for that molecule. The calculated barriers change very little with the level of calculation above the MP2/6-31+G(2df,p) level. Barriers for H atom transfer reactions range from 4.5 to 18.6 kcal/mol and tend to decrease with increasing chlorination of the disilene. Barriers for Cl atom transfer range from 9.1 to 23.3 kcal/mol and also tend to decrease with increasing chlorination of the disilene. There is no experimental information available to compare these results with, but there have been a number of theoretical calculations of the barrier for the H_2SiSiH_2 to H_3SiSiH isomerization. The original work on this reaction by Krogh-Jespersen[6] gave a barrier height of 17.3 kcal/mol (electronic barrier only) at the MP3/6-31G(d,p)//HF6-31G(d,p) level. The BAC-MP4 calculation of Ho and Melius[3] gives a barrier near 25 kcal/mol, substantially higher than our prediction. Ernst et al.[2] calculated a barrier of 19.8 kcal/mol based on a CISD calculation with two reference configurations. Finally, the results of Gordon et al.[5] at the MP4/MC-311G(d,p)//MP2/6-31G(d,p) give a barrier of 16.9 kcal/mol. Our value of 14.6 kcal/mol is close to but

TABLE 5: Isomerization Barriers[a]

		forward barrier					
reaction	ΔH_{rxn}	MP2 6-31G(d,p)	MP2 6-31+G(2df,p)	MP4 6-31+G(2df,p)	G2(MP2)	G2	reverse barrier
$H_2SiSiH_2 \leftrightarrow H_3SiSiH$	7.3	16.9	14.6	15.0	14.7	14.6	7.5
$HClSiSiH_2 \leftrightarrow H_2ClSiSiH^c$	4.8	25.8	22.0	22.2	22.3	22.2	17.4
$HClSiSiH_2 \leftrightarrow H_3SiSiCl$	−2.5	16.2	18.6	16.2	16.4	15.9	18.6
$HClSiSiH_2 \leftrightarrow H_2ClSiSiH^b$	4.8	9.3	7.0	7.7	7.4	7.3	2.6
$Cl_2SiSiH_2 \leftrightarrow H_2ClSiSiCl$	−1.9	26.9	23.6	23.7	23.3	23.3	25.2
cis-$HClSiSiHCl \leftrightarrow H_2ClSiSiCl$	−5.0	10.8	8.5	9.0	8.9	8.8	13.9
trans-$HClSiSiHCl \leftrightarrow H_2ClSiSiCl$	−5.4	12.9	9.9	10.4	10.6	10.5	16.0
trans-$HClSiSiHCl \leftrightarrow HCl_2SiSiH$	−0.5	16.1	12.3	12.8	13.4	13.2	13.7
cis-$HClSiSiHCl \leftrightarrow HCl_2SiSiH$	−0.1	19.6	15.7	16.2	16.3	16.1	16.3
$Cl_2SiSiH_2 \leftrightarrow HCl_2SiSiH$	3.1	6.5	3.9	4.7	4.6	4.5	1.5
$Cl_2SiSiHCl \leftrightarrow Cl_3SiSiH$	−0.7	13.0	9.6	10.1	10.8		11.7
$Cl_2SiSiHCl \leftrightarrow HCl_2SiSiCl^b$	−5.7	7.7	5.0	5.7	5.9		11.7
$Cl_2SiSiHCl \leftrightarrow HCl_2SiSiCl^c$	−5.7	17.3	14.0	14.3	14.5		20.3
$Cl_2SiSiCl_2 \leftrightarrow Cl_3SiSiCl$	−8.4	11.4	9.1				17.6

[a] Energies are in kcal/mol. ΔH_{rxn} is the standard heat of reaction at 298 K. Forward and reverse reaction barriers are at 0 K, including zero-point energy. Entries left blank were not calculated because of computational expense. [b] Transition state corresponding to H atom transfer. [c] Transition state corresponding to Cl atom transfer.

lower than the results of Gordon et al. The decrease appears to be due to the additional polarization and diffuse functions included in the basis sets used in this study. This is also demonstrated by the decrease in the calculated barrier between the MP2/6-31G(d,p) and MP2/6-31+G(2df,p) levels of calculation (see Table 5). We are not aware of any previous studies of the other isomerizations considered here.

We also located and characterized a transition state for the cis-to-trans isomerization of HClSiSiHCl. The transition state located was not symmetric, having the H and Cl at one end nearly in a plane with the silicon atoms and those at the other end bent nearly 90° out of that plane. At the G2 level, the isomerization barrier was 13.5 kcal/mol (12.6 kcal/mol at the MP2/6-31+G(2df,p)//MP2/6-31G(d,p) level), which is comparable to the barriers for the other isomerizations considered here. For comparison, we considered the barriers for rotation about the Si−Si bond of H_2SiSiH_2 and $Cl_2SiSiCl_2$ through a similar transition state. At the G2 level, the rotational barrier for H_2SiSiH_2 was 25.7 kcal/mol (25.0 kcal/mol at the MP2/6-31+G(2df,p)//MP2/6-31G(d,p) level). The rotational barrier for $Cl_2SiSiCl_2$ was 13.9 kcal/mol at the MP2/6-31+G(2df,p)//MP2/6-31G(d,p) level. These barriers are all comparable to or higher than barriers for disilene-to-silylsilylene isomerizations.

Decomposition of the Disilenes to Silylenes. To confirm that dimerization of two chlorinated silylenes to a disilene is barrierless and to get an idea of the shape of the potential surface on which these reactions take place, we carried out relaxed potential energy surface scans for this process. For each of the dimerizations the geometry was optimized at the HF/6-31G(d) level with the Si−Si bond distance held fixed at values ranging from the equilibrium bond distance to 2 Å longer than the equilibrium bond distance. Energies at the MP2/6-31+G(2df,p) level were then computed at each of these geometries. The results of these calculations are presented in Figure 2. The energies presented are relative to the separated silylenes and include electronic energy only. Note that these energy profiles do not follow an intrinsic reaction coordinate, but simply show the change in energy as the Si−Si bond length is extended along a particular path. For H_2SiSiH_2, Cl_2SiSiH_2, and $Cl_2SiSiCl_2$ dissociation, the path followed maintains C_s symmetry, with the plane of symmetry containing the two silicon atoms. For *cis*-HClSiSiHCl dissociation, the path maintains C_2 symmetry. The results in Figure 2 show that all of the dimerizations are, in fact, barrierless and would be expected to proceed through loose transition states with Si−Si bond distances on the order of 3.5−4 Å.

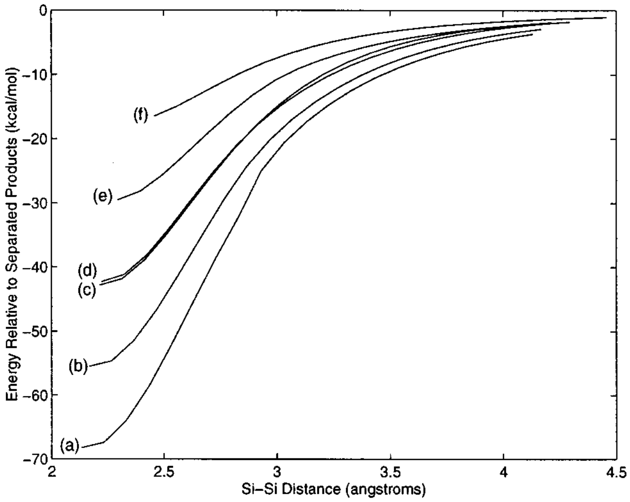

Figure 2. Energies along the path for decomposition of disilenes to pairs of silylenes as described in the text. Starting from the bottom of the figure, curves correspond to (a) $H_2SiSiH_2 \rightarrow 2SiH_2$, (b) $HClSiSiH_2 \rightarrow SiHCl + SiH_2$, (c) $HClSiSiHCl \rightarrow 2SiHCl$, (d) $Cl_2SiSiH_2 \rightarrow SiCl_2 + SiH_2$, (e) $Cl_2SiSiHCl \rightarrow SiCl_2 + SiHCl$, and (f) $Cl_2SiSiCl_2 \rightarrow 2SiCl_2$.

Comparison of Energies of $Si_2H_nCl_{4-n}$ Isomers and Potential Decomposition Products. Using results from this study and previous theoretical and experimental studies, we can consider the relative energies of the various $Si_2H_nCl_{4-n}$ isomers and their decomposition products. Table 6 compares the 298 K standard enthalpies of formation of the silylsilylene, disilene, and dibridged isomers and several potential sets of decomposition products. We see that while disilene is predicted to be lower in energy than silylsilylene, the lowest energy isomer for all of the chlorinated species is the silylsilylene isomer with a chlorine bound to the divalent silicon ($H_nCl_{3-n}SiSiCl$). However, the energy differences between the silylsilylene and disilene structures are small in all cases, with no more than 8.5 kcal/mol between the highest and lowest energy disilene and silylsilylene structures for any of these stoichiometries. The dibridged structures are consistently higher in energy than the disilenes or silylsilylenes, but are still significantly bound relative to a pair of silylenes. Structures with bridging hydrogen atoms are lower in energy than those with bridging chlorine atoms.

TABLE 6: Comparison of Enthalpies of Isomers and Decomposition Products[h]

Si_2H_4	$\Delta H_f{}^{\circ}{}_{298}$	Si_2H_3Cl	$\Delta H_f{}^{\circ}{}_{298}$	$Si_2H_2Cl_2$	$\Delta H_f{}^{\circ}{}_{298}$	Si_2HCl_3	$\Delta H_f{}^{\circ}{}_{298}$	Si_2Cl_4	$\Delta H_f{}^{\circ}{}_{298}$
H_2SiSiH_2[a]	68.1	$H_3SiSiCl$[b]	26.8	$H_2ClSiSiCl$[b]	−14.6	$HCl_2SiSiCl$[b]	−58.5	$Cl_3SiSiCl$[b]	−102.8
H_3SiSiH[b]	75.4	$HClSiSiH_2$a	29.3	Cl_2SiSiH_2[a]	−12.7	Cl_3SiSiH[b]	−53.5	$Cl_2SiSiCl_2$[a]	−94.3
HSiHHSiH[a]	89.0	$H_2ClSiSiH$[b]	34.1	HCl_2SiSiH[b]	−9.6	$Cl_2SiSiHCl$[a]	−52.8	ClSiClClSiCl[a]	−86.9
SiHHSi[d] + H_2	91.8	ClSiHHSiH[a]	42.5	*cis*-HClSiSiHCl[a]	−9.6	ClSiHClSiCl[a]	−48.4	$SiCl_2$[c] + $SiCl_2$[c]	−77.2
HSiHSi[d] + H_2	101.3	HSiClHSiH[a]	48.4	*trans*-HClSiSiHCl[a]	−9.1	ClSiClClSiH[a]	−38.7	$SiCl_4$[e] + $Si(^3P)$[e]	−50.8
H_2SiSi[d] + H_2	104.2	SiH_3Cl[c] + $Si(^3P)$[e]	75.6	ClSiHHSiCl[a]	−1.6	$SiCl_2$[c] + SiHCl[c]	−23.6	$SiCl_3$[c] + SiCl[c]	−39.3
HSiSiH[d] + H_2	112.2	SiHCl[c] + SiH_2[f]	80.2	ClSiClHSiH[a]	1.1	$SiHCl_3$[c] + $Si(^3P)$[e]	−9.2	$SiCl_4$[e] + $Si(^1D)$[e]	−32.8
SiH_4[e] + $Si(^3P)$[e]	115.8	SiH_3[e] + SiCl[c]	84.4	HSiClClSiH[a]	13.1	$SiHCl_2$[c] + SiCl[c]	2.5		
SiH_2[f] + SiH_2[f]	130.4	SiH_3Cl[c] + $Si(^1D)$[e]	93.6	SiH_2[f] + $SiCl_2$[c]	26.6	$SiHCl_3$[c] + $Si(^1D)$[e]	8.8		
SiH_4[e] + $Si(^1D)$[e]	133.8	SiH_2Cl[c] + SiH[g]	97.6	SiHCl[c] + SiHCl[c]	30.0	$SiCl_3$[c] + SiH[g]	13.8		
SiH_3[e] + SiH[g]	137.5			SiH_2Cl_2[c] + $Si(^3P)$[e]	33.4				
				SiH_2Cl[c] + SiCl[c]	44.5				
				SiH_2Cl_2[c] + $Si(^1D)$[e]	51.4				
				$SiHCl_2$[c] + SiH[g]	55.6				

[a] This work. [b] Reference 1. [c] Reference 25. [d] Reference 8. [e] Reference 26. [f] Reference 28. [g] Reference 30. [h] Heats of formation are in kcal/mol at 298 K and 1 bar.

There are several possible decomposition paths for the $Si_2H_nCl_{4-n}$ species, and energies for some of the most likely products are shown in Table 6. As seen above, the disilenes can dissociate to pairs of silylenes with an activation barrier given by heat of reaction. Likewise, the silylsilylenes can dissociate to SiH_nCl_{3-n} + SiCl or $SiH_{n-1}Cl_{4-n}$ + SiH by a simple bond cleavage that would be expected to have no barrier other than the heat of reaction. The silylsilylenes could also eliminate silicon atoms. Sakai et al.[31] calculated barriers for the elimination of silicon atoms from H_3SiSiH on both the singlet and the triplet surfaces. Their calculations predicted that there was essentially no barrier for insertion of $Si(^1D)$ into silane, but that there was a barrier of about 7 kcal/mol for insertion of ground-state $Si(^3P)$ into silane. The calculations of Katzer et al.[7] place triplet silylsilylene 12 kcal/mol above the singlet. Singlet−triplet splitting increases with substitution of electronegative substituents on silylenes,[31] so we would expect this splitting to be larger for the chlorinated species. Thus, silicon elimination could occur on either the singlet or triplet surface, or a combination thereof, but presumably has an activation energy beyond the heat of reaction for production of ground-state silicon atoms ($Si(^3P)$). Finally, either the disilenes or silylsilylenes could possibly eliminate hydrogen. The energetics for production of several Si_2H_2 structures by hydrogen elimination from Si_2H_4 are included in Table 6 for reference. These paths presumably have energetic barriers in addition to the heat of reaction, but a separate study would be required to confirm this. Likewise, a separate study would be required to determine energetics for Si_2HCl and Si_2Cl_2 isomers and hydrogen elimination paths that might produce them from the chlorinated disilenes and silylsilylenes.

Examination of Table 6 shows that the endothermicities of reactions that produce SiH, SiCl, and Si atoms remain roughly constant with chlorine substitution, while the endothermicity for decomposition to a pair of silylenes decreases dramatically. For reactions producing SiH, the endothermicity increases from 62 kcal/mol for $H_3SiSiH \rightarrow SiH_3 + SiH$ to 67 kcal/mol for $Cl_3SiSiH \rightarrow SiCl_3 + SiH$. Likewise, for reactions producing SiCl, the endothermicity increases from 58 kcal/mol for $H_3SiSiCl \rightarrow SiH_3 + SiCl$ to 64 kcal/mol for $Cl_3SiSiCl \rightarrow SiCl_3 + SiCl$. The endothermicity for elimination of silicon atoms changes little with chlorine substitution and is near 50 kcal/mol for elimination of $Si(^3P)$ from $H_nCl_{3-n}SiSiCl$ and near 42 kcal/mol for elimination of $Si(^3P)$ from $H_nCl_{3-n}SiSiH$. The endothermicity for decomposition of a disilene to a pair of silylenes, however, decreases from 62 kcal/mol for $H_2SiSiH_2 \rightarrow 2\,SiH_2$ to only 17 kcal/mol for $Cl_2SiSiCl_2 \rightarrow 2SiCl_2$. These reaction energetics show that for Si_2H_4 and Si_2H_3Cl decomposition there is no path that is clearly preferred on energetic grounds, but that for $Si_2H_2Cl_2$, Si_2HCl_3, and Si_2Cl_4 decomposition to silylenes should be much faster than the other possible paths. Also, we note that the isomerization barriers between the disilenes and silylsilylenes are smaller than the barriers for decomposition, so the isomerization reactions will be much faster than the decompositions and, in the absence of fast bimolecular reactions, will serve to maintain an equilibrium between the various isomers regardless of which isomer is produced initially by other reactions.

Summary and Conclusions

Structures, vibrational frequencies, and energies have been presented for the chlorinated disilenes, their dibridged isomers, and the transition states connecting the chlorinated disilenes and silylsilylenes. The silylsilylene isomer with the structure $H_nCl_{3-n}SiSiCl$ is found to be the lowest energy structure for all of the chlorinated compounds. The dibridged structures are all significantly higher in energy than the silylsilylene and disilene structures. Isomerization barriers for H-transfer reactions range from 5 to 18 kcal/mol above the disilene, while those for isomerization by chlorine transfer range from 9 to 23 kcal/mol above the disilene. Energies along paths for decomposition of the chlorinated disilenes to silylenes have been presented, confirming that these reactions have no barrier beyond the heat of reaction. Finally, energetics of various decomposition products of the $Si_2H_nCl_{4-n}$ compounds have been considered. It has been shown that for the species with two or more chlorines, decomposition to silylenes should be the dominant reaction path based on the energetics of competing paths. The isomerization barriers are much smaller than decomposition barriers, so the isomerization reactions will be fast and serve to maintain an equilibrium between the silylsilylene and disilene isomers.

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