Supporting Information

Theoretical Study for the Si/C-mixed Benzenes and their Major Valence Isomers

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1. Geometric data of five types of the Si/C-mixed benzene isomers, $C_{6-n}Si_nH_6$ (n = 0-6), with the molecular symmetry (point group) at the CCSD/cc-pVDZ level are collected in Tables S1-S5

Table S1. Geometrical parameters (r / Å), point group (p. g.) and planarity of benzene-type isomers.

molecule (Si position)	r_{1-2}	r_{2-3}	r_{3-4}	r_{4-5}	r_{5-6}	r_{6-1}	p. g.	planarity
C_6H_6 (-)	1.406	1.406	1.406	1.406	1.406	1.406	D_{6h}	planar
C_5SiH_6 (1)	1.785	1.410	1.412	1.412	1.410	1.785	C_{2v}	planar
$C_4Si_2H_6$ (1,2)	2.185	1.815	1.398	1.431	1.398	1.815	C_{2v}	planar
$C_4Si_2H_6$ (1,3)	1.779	1.779	1.789	1.414	1.414	1.789	C_{2v}	planar
$C_4Si_2H_6$ (1,4)	1.800	1.411	1.800	1.800	1.411	1.800	D_{2h}	planar
$C_3Si_3H_6$ (1,2,3)	2.214	2.214	1.798	1.412	1.412	1.798	C_{2v}	planar
$C_3Si_3H_6$ (1,2,4)	2.201	1.803	1.771	1.816	1.397	1.828	C_s	planar
$C_3Si_3H_6$ (1,3,5)	1.779	1.779	1.779	1.779	1.779	1.779	D_{3h}	planar
$C_2Si_4H_6$ (1,2,3,4)	2.216	2.254	2.216	1.831	1.393	1.831	C_2	buckled
$C_2Si_4H_6$ (1,2,3,5)	2.254	2.254	1.784	1.783	1.783	1.784	C_s	buckled
$C_2Si_4H_6$ (1,2,4,5)	2.228	1.793	1.793	2.228	1.793	1.793	D_{2h}	planar
CSi_5H_6 (1,2,3,4,5)	2.246	2.244	2.244	2.246	1.790	1.790	C_s	buckled
Si_6H_6 (1,2,3,4,5,6)	2.248	2.248	2.248	2.248	2.248	2.248	D_{3d}	buckled

Table S2. Geometrical parameters (r / Å), point group (p. g.) and planarity of fulvene-type isomers.

molecule (Si position)	r_{1-2}	r_{2-3}	r_{3-4}	r_{4-5}	r_{5-6}	r_{6-2}	p. g.	planarity
C_6H_6 (-)	1.354	1.487	1.363	1.490	1.363	1.487	C_{2v}	planar
C_5SiH_6 (1)	1.743	1.478	1.371	1.477	1.371	1.478	C_{2v}	planar
C_5SiH_6 (2)	1.726	1.871	1.364	1.500	1.364	1.364	C_{2v}	planar
C_5SiH_6 (3)	1.356	1.887	1.746	1.484	1.371	1.482	C_s	planar
C_5SiH_6 (4)	1.362	1.478	1.744	1.868	1.365	1.496	C_s	planar
$C_4Si_2H_6$ (1,2)	2.193	1.877	1.365	1.495	1.365	1.877	C_s	buckled
$C_4Si_2H_6$ (1,3)	1.738	1.871	1.753	1.467	1.383	1.467	C_1	buckled
$C_4Si_2H_6$ (1,4)	1.759	1.461	1.756	1.854	1.373	1.488	C_s	planar
$C_4Si_2H_6$ (2,3)	1.732	2.306	1.757	1.487	1.372	1.870	C_1	buckled
$C_4Si_2H_6$ (2,4)	1.729	1.844	1.738	1.881	1.368	1.892	C_s	planar
$C_4Si_2H_6$ (3,4)	1.359	1.918	2.215	1.886	1.368	1.487	C_1	buckled
$C_4Si_2H_6$ (3,5)	1.365	1.886	1.743	1.847	1.754	1.472	C_s	planar
$C_4Si_2H_6$ (3,6)	1.358	1.897	1.813	1.422	1.813	1.897	C_2	buckled
$C_4Si_2H_6$ (4,5)	1.368	1.484	1.755	2.286	1.755	1.484	C_{2v}	planar
$C_3Si_3H_6$ (1,2,3)	2.194	2.311	1.764	1.478	1.375	1.875	C_1	buckled
$C_3Si_3H_6$ (1,2,4)	2.206	1.845	1.741	1.876	1.368	1.901	C_1	buckled
$C_3Si_3H_6$ (1,3,4)	1.744	1.902	2.229	1.875	1.377	1.475	C_1	buckled
$C_3Si_3H_6$ (1,3,5)	1.757	1.870	1.751	1.829	1.770	1.454	C_s	planar
$C_3Si_3H_6$ (1,3,6)	1.728	1.870	1.823	1.411	1.823	1.870	C_2	buckled
$C_3Si_3H_6$ (1,4,5)	1.768	1.468	1.768	2.266	1.768	1.468	C_{2v}	planar
$C_3Si_3H_6$ (2,3,4)	1.735	2.334	2.216	1.885	1.369	1.891	C_1	buckled
$C_3Si_3H_6$ (2,3,5)	1.736	2.332	1.752	1.846	1.748	1.832	C_s	planar
$C_3Si_3H_6$ (2,3,6)	1.741	2.332	1.810	1.432	1.810	2.332	C_2	buckled
$C_3Si_3H_6$ (2,4,5)	1.735	1.857	1.747	2.315	1.747	1.857	C_{2v}	planar
$C_3Si_3H_6$ (3,4,5)	1.367	1.899	2.204	2.323	1.760	1.472	C_1	buckled
$C_3Si_3H_6$ (3,4,6)	1.361	1.943	2.265	1.839	1.750	1.867	C_1	buckled
$C_2Si_4H_6$ (1,2,3,4)	2.205	2.340	2.228	1.876	1.372	1.896	C_1	buckled
$C_2Si_4H_6$ (1,2,3,5)	2.211	2.338	1.755	1.836	1.755	1.831	C_1	buckled

$C_2Si_4H_6$ (1,2,3,6)	-	-	-	-	-	-	-	-
$C_2Si_4H_6$ (1,2,4,5)	2.202	1.856	1.751	2.308	1.751	1.856	C_s	buckled
$C_2Si_4H_6$ (1,3,4,5)	1.761	1.879	2.231	2.313	1.777	1.455	C_1	buckled
$C_2Si_4H_6$ (1,3,4,6)	1.735	1.932	2.279	1.827	1.758	1.835	C_1	buckled
$C_2Si_4H_6$ (2,3,4,5)	1.738	2.330	2.187	2.321	1.750	1.847	C_1	buckled
$C_2Si_4H_6$ (2,3,4,6)	1.745	2.359	2.282	1.828	1.763	2.332	C_1	buckled
$C_2Si_4H_6$ (3,4,5,6)	1.363	1.901	2.211	2.332	2.211	1.901	C_2	buckled
CSi_5H_6 (1,2,3,4,5)	2.203	2.332	2.200	2.315	1.756	1.846	C_1	buckled
CSi_5H_6 (1,2,3,4,6)	-	-	-	-	-	-	-	-
CSi_5H_6 (1,3,4,5,6)	1.739	1.874	2.223	2.333	2.223	1.874	C_2	buckled
CSi_5H_6 (2,3,4,5,6)	1.743	2.339	2.216	2.310	2.216	2.339	C_2	buckled
Si_6H_6 (1,2,3,4,5,6)	-	-	-	-	-	-	-	-

Table S3. Geometrical parameters (r / Å) and point group (p. g.) of Dewar-benzene-type isomers.

molecule (Si position)	r_{1-2}	r_{2-3}	r_{3-4}	r_{4-5}	r_{5-6}	r_{6-1}	r_{1-4}	p. g.
C_6H_6 (-)	1.539	1.356	1.539	1.539	1.356	1.539	1.584	C_{2v}
C_5SiH_6 (1)	1.902	1.365	1.548	1.548	1.365	1.902	1.915	C_s
C_5SiH_6 (2)	1.913	1.737	1.542	1.541	1.355	1.533	1.604	C_1
$C_4Si_2H_6$ (1,2)	2.341	1.761	1.541	1.551	1.362	1.899	1.943	C_1
$C_4Si_2H_6$ (1,3)	1.883	1.745	1.902	1.541	1.365	1.904	1.951	C_1
$C_4Si_2H_6$ (1,4)	1.933	1.371	1.933	1.933	1.371	1.933	2.304	C_{2v}
$C_4Si_2H_6$ (2,3)	1.942	2.197	1.943	1.528	1.356	1.533	1.614	C_1
$C_4Si_2H_6$ (2,5)	1.927	1.738	1.539	1.927	1.738	1.539	1.613	C_2
$C_4Si_2H_6$ (2,6)	1.900	1.732	1.548	1.548	1.732	1.900	1.622	C_s
$C_3Si_3H_6$ (1,2,3)	2.351	2.190	1.914	1.543	1.363	1.897	1.960	C_1
$C_3Si_3H_6$ (1,2,4)	2.369	1.759	1.893	1.938	1.370	1.926	2.337	C_1
$C_3Si_3H_6$ (1,2,5)	2.352	1.761	1.540	1.913	1.742	1.882	1.972	C_1
$C_3Si_3H_6$ (1,2,6)	2.329	1.753	1.547	1.547	1.753	2.329	1.973	C_s
$C_3Si_3H_6$ (1,3,5)	1.889	1.739	1.889	1.889	1.739	1.889	1.989	C_s
$C_3Si_3H_6$ (2,3,5)	1.963	2.209	1.924	1.911	1.739	1.536	1.618	C_1
$C_2Si_4H_6$ (1,2,3,4)	2.356	2.189	2.356	1.929	1.369	1.929	2.350	C_s
$C_2Si_4H_6$ (1,2,3,5)	2.366	2.192	1.905	1.896	1.737	1.888	1.987	C_1
$C_2Si_4H_6$ (1,2,3,6)	2.348	2.183	1.927	1.544	1.757	2.339	1.978	C_1
$C_2Si_4H_6$ (1,2,4,5)	2.380	1.759	1.887	2.380	1.759	1.887	2.367	C_2
$C_2Si_4H_6$ (1,2,4,6)	2.349	1.752	1.902	1.902	1.752	2.349	2.377	C_s
$C_2Si_4H_6$ (2,3,5,6)	1.934	2.198	1.940	1.940	2.198	1.934	1.623	C_s
CSi_5H_6 (1,2,3,4,5)	2.371	2.186	2.345	2.358	1.753	1.894	2.384	C_s
CSi_5H_6 (1,2,3,5,6)	2.360	2.186	1.912	1.912	2.186	2.360	1.985	C_1
Si_6H_6 (1,2,3,4,5,6)	2.355	2.179	2.355	2.355	2.179	2.355	2.393	C_{2v}

Table S4. Geometrical parameters (r / Å) and point group (p. g.) of benzvalene-type isomers.

molecule (Si position)	r_{1-2}	r_{2-3}	r_{3-4}	r_{3-6}	r_{4-5}	r_{5-6}	r_{5-1}	r_{4-6}	p. g.
C_6H_6 (-)	1.352	1.521	1.534	1.534	1.534	1.534	1.521	1.470	C_{2v}
C_5SiH_6 (1)	1.735	1.530	1.532	1.532	1.540	1.540	1.905	1.473	C_s
C_5SiH_6 (3)	1.360	1.881	1.873	1.873	1.538	1.538	1.518	1.540	C_s
C_5SiH_6 (4)	-	-	-	-	-	-	-	-	-
$C_4Si_2H_6$ (1,2)	2.223	1.935	1.539	1.539	1.539	1.539	1.935	1.477	C_2
$C_4Si_2H_6$ (1,3)	1.737	1.866	1.877	1.877	1.549	1.549	1.895	1.542	C_s

$C_4Si_2H_6$ (1,4)	-	-	-	-	-	-	-	-	-
$C_4Si_2H_6$ (1,5)	1.751	1.519	1.536	1.536	1.883	1.883	2.310	1.538	C_s
$C_4Si_2H_6$ (3,4)	1.375	1.860	2.482	1.831	2.181	1.444	1.486	2.238	C_1
$C_4Si_2H_6$ (3,5)	1.367	1.897	1.875	1.875	1.875	1.875	1.897	1.611	C_{2v}
$C_4Si_2H_6$ (4,6)	1.367	1.503	1.972	1.972	1.972	1.972	1.503	2.522	C_{2v}
$C_3Si_3H_6$ (1,2,3)	2.231	2.362	1.875	1.894	1.549	1.538	1.892	1.534	C_1
$C_3Si_3H_6$ (1,2,4)	-	-	-	-	-	-	-	-	-
$C_3Si_3H_6$ (1,3,4)	1.756	1.830	2.554	1.823	2.149	1.461	1.855	2.197	C_1
$C_3Si_3H_6$ (1,3,5)	1.749	1.870	1.877	1.877	1.886	1.886	2.330	1.605	C_s
$C_3Si_3H_6$ (1,4,5)	1.793	1.459	2.295	1.435	2.515	1.846	2.291	2.233	C_1
$C_3Si_3H_6$ (1,4,6)	1.748	1.522	1.968	1.968	1.970	1.970	1.886	2.503	C_s
$C_3Si_3H_6$ (3,4,5)	1.371	1.889	2.398	1.837	2.398	1.837	1.889	2.336	C_s
$C_3Si_3H_6$ (3,4,6)	1.369	1.885	2.360	2.360	1.972	1.972	1.505	2.687	C_s
$C_2Si_4H_6$ (1,2,3,4)	-	-	-	-	-	-	-	-	-
$C_2Si_4H_6$ (1,2,3,5)	2.184	2.339	1.878	1.884	1.884	1.878	2.339	1.606	C_2
$C_2Si_4H_6$ (1,2,4,6)	2.235	1.928	1.954	1.939	1.939	1.954	1.928	2.485	C_2
$C_2Si_4H_6$ (1,3,4,5)	1.759	1.853	2.436	1.831	2.410	1.850	2.320	2.279	C_1
$C_2Si_4H_6$ (1,3,4,6)	1.743	1.869	2.374	2.374	1.977	1.977	1.873	2.662	C_s
$C_2Si_4H_6$ (1,4,5,6)	1.763	1.506	1.976	1.976	2.380	2.380	2.314	2.671	C_s
$C_2Si_4H_6$ (3,4,5,6)	1.369	1.899	2.361	2.361	2.361	2.361	1.899	2.910	C_{2v}
CSi_5H_6 (1,2,3,4,5)	2.192	2.326	2.411	1.843	2.418	1.842	2.317	2.271	C_1
CSi_5H_6 (1,2,3,4,6)	2.256	2.366	2.361	2.394	1.997	1.971	1.859	2.243	C_1
CSi_5H_6 (1,3,4,5,6)	1.753	1.869	2.374	2.374	2.375	2.375	2.330	2.883	C_s
Si_6H_6 (1,2,3,4,5,6)	2.179	2.336	2.374	2.373	2.373	2.374	2.336	2.878	C_2

Table S5. Geometrical parameters (r / Å) and point group (p. g.) of prismane-type isomers.

molecule (Si position)	r_{1-2}	r_{2-3}	r_{3-1}	r_{4-5}	r_{5-6}	r_{6-4}	r_{1-4}	r_{2-5}	r_{3-6}	p. g.
C_6H_6 (-)	1.534	1.534	1.534	1.534	1.534	1.534	1.567	1.567	1.567	D_{3h}
C_5SiH_6 (1)	1.892	1.597	1.892	1.544	1.528	1.544	1.928	1.564	1.564	C_s
$C_4Si_2H_6$ (1,2)	2.298	1.948	1.948	1.557	1.537	1.537	1.932	1.932	1.572	C_s
$C_4Si_2H_6$ (1,4)	1.914	1.574	1.914	1.914	1.574	1.914	2.363	1.566	1.566	C_{2v}
$C_4Si_2H_6$ (1,5)	1.901	1.605	1.891	1.901	1.891	1.605	1.917	1.917	1.558	C_2
$C_3Si_3H_6$ (1,2,3)	2.370	2.370	2.370	1.546	1.546	1.546	1.948	1.948	1.948	C_{3v}
$C_3Si_3H_6$ (1,2,4)	2.313	1.920	1.996	1.927	1.576	1.915	2.359	1.917	1.566	C_1
$C_3Si_3H_6$ (1,2,6)	2.295	1.961	1.961	1.618	1.894	1.894	1.925	1.925	1.904	C_s
$C_2Si_4H_6$ (1,2,3,4)	2.392	2.355	2.392	1.910	1.595	1.910	2.371	1.939	1.939	C_s
$C_2Si_4H_6$ (1,2,4,5)	2.329	1.955	1.955	2.329	1.955	1.955	2.367	2.367	1.590	C_{2v}
$C_2Si_4H_6$ (1,2,4,6)	2.303	1.926	2.006	2.006	1.926	2.303	2.368	1.908	1.908	C_2
CSi_5H_6 (1,2,3,4,5)	2.435	2.363	2.363	2.321	1.958	1.958	2.370	2.370	1.931	C_s
Si_6H_6 (1,2,3,4,5,6)	2.389	2.389	2.389	2.389	2.389	2.389	2.392	2.392	2.392	D_{3h}

2. The quantity of π-electrons assigned to each skeletal atom of BE-type isomers

Table S6. π electron quantity assigned to each skeletal atom at the CCSD/cc-pVDZ.

molecule (Si position)	point group	planarity	1	2	3	4	5	6	sum
C_6H_6	D_{6h}	planar	0.994	0.994	0.994	0.994	0.994	0.994	5.967
C_5SiH_6 (1)	C_{2v}	planar	0.746	1.129	0.953	1.046	0.953	1.129	5.958
$C_4Si_2H_6$ (1,2)	C_{2v}	planar	0.918	0.918	1.069	1.069	0.986	0.986	5.945
$C_4Si_2H_6$ (1,3)	C_{2v}	planar	0.673	1.300	0.673	1.197	0.906	1.197	5.945
$C_4Si_2H_6$ (1,4)	D_{2h}	planar	0.820	1.078	1.078	0.820	1.078	1.078	5.949
$C_3Si_3H_6$ (1,2,3)	C_{2v}	planar	0.823	1.072	0.823	1.140	0.935	1.140	5.932
$C_3Si_3H_6$ (1,2,4)	C_s	planar	1.003	0.846	1.262	0.713	1.104	1.006	5.934
$C_3Si_3H_6$ (1,3,5)	D_{3h}	planar	0.603	1.374	0.603	1.374	0.603	1.374	5.931
$C_2Si_4H_6$ (1,2,3,4)	C_2	buckled	0.901	1.009	1.009	0.901	1.050	1.050	5.920
$C_2Si_4H_6$ (1,2,3,5)	C_s	buckled	0.736	1.165	0.736	1.323	0.635	1.323	5.919
$C_2Si_4H_6$ (1,2,4,5)	D_{2h}	planar	0.881	0.881	1.199	0.881	0.881	1.199	5.924
CSi_5H_6 (1,2,3,4,5)	C_s	buckled	0.790	1.077	0.914	1.077	0.790	1.259	5.907
Si_6H_6 (1,2,3,4,5,6)	D_{3d}	buckled	0.982	0.982	0.982	0.982	0.982	0.982	5.895

As the Table shows, $C_3Si_3H_6$(1,2,3) and $C_3Si_3H_6$(1,2,4) take a planar structure even though they have a silicon (2Si and 1Si, respectively) with large (>1.0) π electron quantity. This may be explained from that the relatively small amount of the π electrons on the adjacent Si atoms. Therefore, for the Si/C-mixed benzenes with Si sequence, in addition to the ratio of silicon atoms holding large π electron quantity, that of the neighbors in the chain seems to be also important for the planarity. In addition, the non-planarization mode frequency of $C_3Si_3H_6$ (1,2,3) is a very small value of +4.19 cm^{-1}.

3. Hexasilafulvene

Hexasilafulvene is not an equilibrium structure, and an isomerization pathway to hexasilabenzvalene via more stable intermediates (Int A and Int.B) was found as shown in Figure S1. Int.B is the most stable structure among the five isomers of Si_6H_6 considered here.

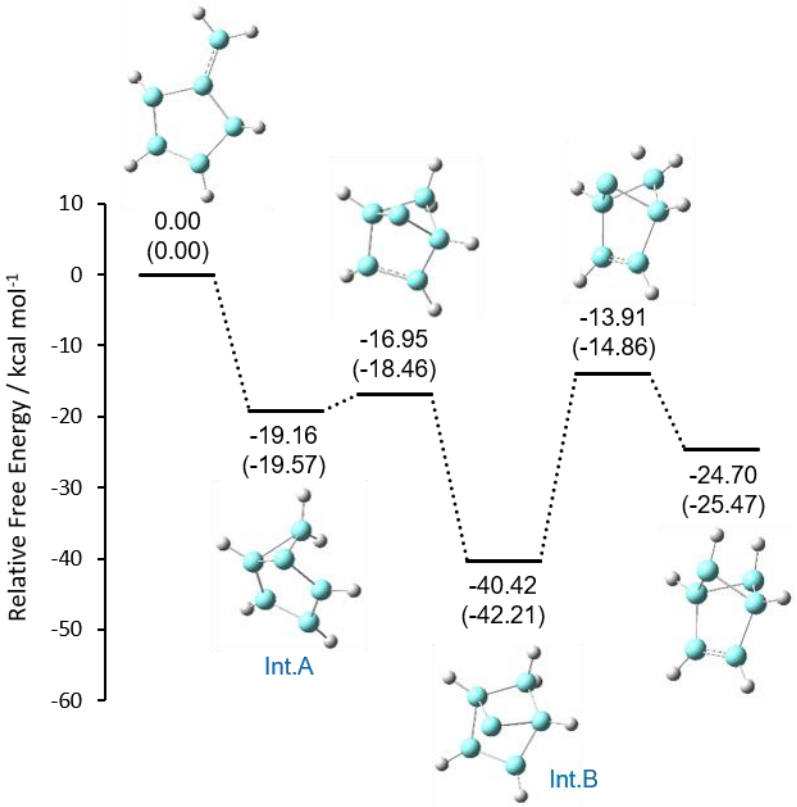

Figure S1. Gibbs free energy profile (kcal mol^{-1}) for the isomerization of hexasilafulvene to hexasilabenzvalene at the CCSD/cc-pVDZ. The values in parentheses are the electronic energies.

4. Relative stability of all possible five types of valence isomers for each Si/C combination of $C_{6-n}Si_nH_6$ (n=0-6) at the CCSD/cc-pVDZ level

Table S7. The relative Gibbs free energies (ΔG) and electronic energies (ΔE) of C_6H_6 isomers.

type	Si position	ΔG (ΔE) / kcal mol^{-1}
BE	(-)	0.00 (0.00)
FL	(-)	29.87 (32.64)
BV	(-)	71.95 (74.13)
DW	(-)	74.43 (77.11)
PR	(-)	113.00 (114.71)

Table S8. The relative Gibbs free energies (ΔG) and electronic energies (ΔE) of C_5SiH_6 isomers.

type	Si position	ΔG (ΔE) / kcal mol^{-1}
BE	(1)	0.00 (0.00)
FL	(1)	21.08 (23.92)
FL	(2)	23.86 (24.91)
FL	(4)	24.63 (26.49)
FL	(3)	28.27 (30.68)
DW	(1)	35.99 (37.38)
BV	(3)	42.14 (42.99)
DW	(2)	63.87 (65.48)
BV	(1)	69.87 (71.50)
PR	(1)	82.23 (83.23)

Table S9. The relative Gibbs free energies (ΔG) and electronic energies (ΔE) of $C_4Si_2H_6$ isomers.

type	Si position	ΔG (ΔE) / kcal mol^{-1}
BE	(1,2)	0.00 (0.00)
BE	(1,3)	0.71 (0.69)
FL	(1,2)	11.64 (13.36)
BE	(1,4)	12.03 (12.42)
BV	(3,4)	14.45 (14.54)
FL	(3,4)	16.61 (17.77)
DW	(1,4)	19.55 (20.00)
BV	(4,6)	21.57 (21.49)
FL	(2,4)	23.83 (25.18)
BV	(3,5)	25.34 (25.67)
FL	(3,5)	25.95 (27.85)
DW	(1,3)	26.52 (27.38)
FL	(1,3)	26.54 (30.14)
FL	(1,4)	27.39 (30.57)
FL	(4,5)	28.28 (29.37)
FL	(2,3)	28.86 (30.31)
FL	(3,6)	33.62 (35.38)
DW	(1,2)	37.17 (37.93)
BV	(1,3)	42.60 (43.34)
DW	(2,3)	47.11 (47.86)
BV	(1,5)	48.93 (49.68)
BV	(1,2)	55.79 (55.98)
PR	(1,2)	57.22 (57.43)
PR	(1,5)	60.86 (60.96)

DW	(2,6)	64.96 (66.26)
PR	(1,4)	67.43 (67.75)
DW	(2,5)	68.36 (69.46)

Table S10. The relative Gibbs free energies (ΔG) and electronic energies (ΔE) of $C_3Si_3H_6$ isomers.

type	Si position	ΔG (ΔE) / kcal mol^{-1}
BE	(1,3,5)	0.00 (0.00)
BE	(1,2,3)	0.50 (2.27)
BV	(3,4,6)	5.49 (5.13)
BV	(3,4,5)	7.39 (7.80)
BE	(1,2,4)	8.57 (10.29)
DW	(1,2,4)	17.22 (17.92)
FL	(1,2,4)	19.99 (22.39)
DW	(1,2,3)	20.17 (20.60)
BV	(1,3,4)	20.61 (21.65)
FL	(2,3,4)	21.67 (22.66)
FL	(3,4,5)	22.29 (23.81)
FL	(3,4,6)	22.61 (24.59)
BV	(1,4,5)	22.75 (23.50)
FL	(1,2,3)	22.90 (25.19)
DW	(1,3,5)	23.94 (25.03)
FL	(1,3,4)	24.51 (27.53)
FL	(2,3,5)	27.26 (28.79)
FL	(2,4,5)	29.26 (30.46)
BV	(1,3,5)	29.61 (30.48)
FL	(1,3,5)	32.19 (36.18)
FL	(1,3,6)	33.72 (37.17)
BV	(1,4,6)	35.62 (37.21)
FL	(2,3,6)	36.70 (37.76)
FL	(1,4,5)	37.53 (41.06)
DW	(1,2,5)	37.60 (38.69)
PR	(1,2,6)	38.07 (38.60)
BV	(1,2,3)	38.35 (38.83)
PR	(1,2,3)	41.24 (40.27)
PR	(1,2,4)	45.70 (46.01)
DW	(1,2,6)	47.09 (48.11)
DW	(2,3,5)	56.60 (58.01)

Table S11. The relative Gibbs free energies (ΔG) and electronic energies (ΔE) of $C_2Si_4H_6$ isomers.

type	Si position	ΔG (ΔE) / kcal mol^{-1}
BV	(3,4,5,6)	0.00 (0.00)
BE	(1,2,3,5)	11.69 (13.88)
BE	(1,2,3,4)	14.97 (16.43)
DW	(1,2,3,4)	15.36 (16.89)
BV	(1,3,4,6)	19.32 (20.89)
BV	(1,3,4,5)	20.28 (22.11)
BE	(1,2,4,5)	21.44 (23.41)
DW	(1,2,4,6)	25.47 (27.18)
FL	(1,2,3,4)	25.56 (28.54)
DW	(1,2,4,5)	26.55 (27.80)
FL	(3,4,5,6)	27.05 (29.32)

BV	(1,4,5,6)	27.06 (28.60)
PR	(1,2,4,6)	28.39 (29.05)
DW	(1,2,3,5)	28.56 (30.34)
FL	(1,2,3,5)	31.13 (34.72)
FL	(2,3,4,6)	31.37 (33.63)
FL	(2,3,4,5)	32.31 (34.73)
BV	(1,2,3,5)	33.50 (34.75)
FL	(1,3,4,6)	33.87 (38.52)
BV	(1,2,4,6)	34.85 (36.76)
FL	(1,2,4,5)	34.88 (38.71)
PR	(1,2,3,4)	35.12 (36.13)
FL	(1,3,4,5)	38.42 (42.97)
DW	(1,2,3,6)	41.56 (43.49)
PR	(1,2,4,5)	42.16 (43.26)
DW	(2,3,5,6)	58.15 (60.65)

Table S12. The relative Gibbs free energies (ΔG) and electronic energies (ΔE) of CSi_5H_6 isomers.

type	Si position	ΔG (ΔE) / kcal mol^{-1}
BV	(1,3,4,5,6)	0.00 (0.00)
BE	(1,2,3,4,5)	8.11 (9.54)
BV	(1,2,3,4,5)	11.01 (12.22)
PR	(1,2,3,4,5)	11.12 (11.01)
DW	(1,2,3,4,5)	12.23 (12.85)
DW	(1,2,3,5,6)	21.17 (22.07)
BV	(1,2,3,4,6)	21.36 (21.99)
FL	(2,3,4,5,6)	23.07 (23.87)
FL	(1,2,3,4,5)	24.45 (27.17)
FL	(1,3,4,5,6)	26.33 (29.55)

Table S13. The relative Gibbs free energies (ΔG) and electronic energies (ΔE) of Si_6H_6 isomers.

type	Si position	ΔG (ΔE) / kcal mol^{-1}
BV	(1,2,3,4,5,6)	0.00 (0.00)
PR	(1,2,3,4,5,6)	1.70 (0.69)
DW	(1,2,3,4,5,6)	9.33 (9.63)
BE	(1,2,3,4,5,6)	10.33 (9.86)

5. Strain energy estimated by homodesmotic reaction energy of the Si/C-mixed prismanes, $C_{6-n}Si_nH_6$ (n=0-6)

<The formula to calculate the homodesmotic reaction energy, ΔE(kcal/mol)>

$C_{6-a}Si_aH_6$(prismane) + b(H_3C-CH_3) + c(H_3C-SiH_3) + d(H_3Si-SiH_3) = e[$(CH_3)_3CH$] + f[$(CH_3)_2(SiH_3)CH$] + g[$(CH_3)(SiH_3)_2CH$] + h[$(SiH_3)_3CH$] + i[$(CH_3)_3SiH$] + j[$(CH_3)_2(SiH_3)SiH$] + k[$(CH_3)(SiH_3)_2SiH$] + l[$(SiH_3)_3SiH$] + ΔE

Table S14. Coefficient and homodesmotic reaction energy (ΔE) of the Si/C-mixed prismanes at the CCSD/cc-pVDZ level.

molecule	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	ΔE / kcal mol^{-1}
C_6H_6	0	9	0	0	6	0	0	0	0	0	0	0	155.5
C_5SiH_6 (1)	1	6	3	0	2	3	0	0	1	0	0	0	145.1
$C_4Si_2H_6$ (1,2)	2	4	4	1	1	2	1	0	0	2	0	0	133.9
$C_4Si_2H_6$ (1,4)	2	4	4	1	0	4	0	0	0	2	0	0	139.7
$C_4Si_2H_6$ (1,5)	2	3	6	0	0	2	2	0	2	0	0	0	139.8
$C_3Si_3H_6$ (1,2,6)	3	1	7	1	0	0	2	1	1	2	0	0	132.7
$C_3Si_3H_6$ (1,2,4)	3	2	5	2	0	1	2	0	0	2	1	0	130.0
$C_3Si_3H_6$ (1,2,3)	3	3	3	3	0	3	0	0	0	0	3	0	121.6
$C_2Si_4H_6$ (1,2,4,6)	4	0	6	3	0	0	0	2	0	2	2	0	124.3
$C_2Si_4H_6$ (1,2,3,4)	4	1	4	4	0	0	2	0	0	1	2	1	120.8
$C_2Si_4H_6$ (1,2,4,5)	4	1	4	4	0	0	2	0	0	0	4	0	125.2
CSi_5H_6 (1,2,3,4,5)	5	0	3	6	0	0	0	1	0	0	3	2	115.3
Si_6H_6 (1,2,3,4,5,6)	6	0	0	9	0	0	0	0	0	0	0	6	108.2

6. Reactivity for the addition reactions

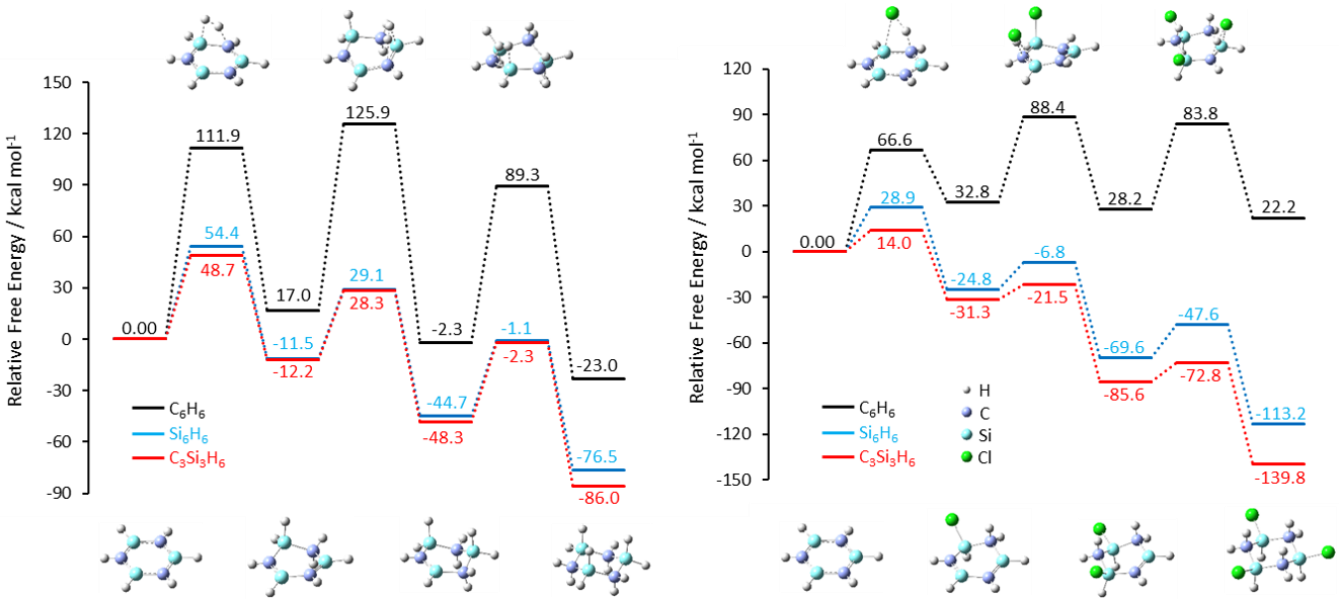

Figure S2. Gibbs free energy profiles (kcal mol^{-1}) of hydrogenation reaction (left) and hydrogen chloride addition reaction (right) of C_6H_6, Si_6H_6, and $C_3Si_3H_6$ at the MP2/cc-pVDZ level.

7. Substituent effects for the geometry of the 6-membered ring and the frontier MOs of the 1,3,5-trisilabenzene derivatives

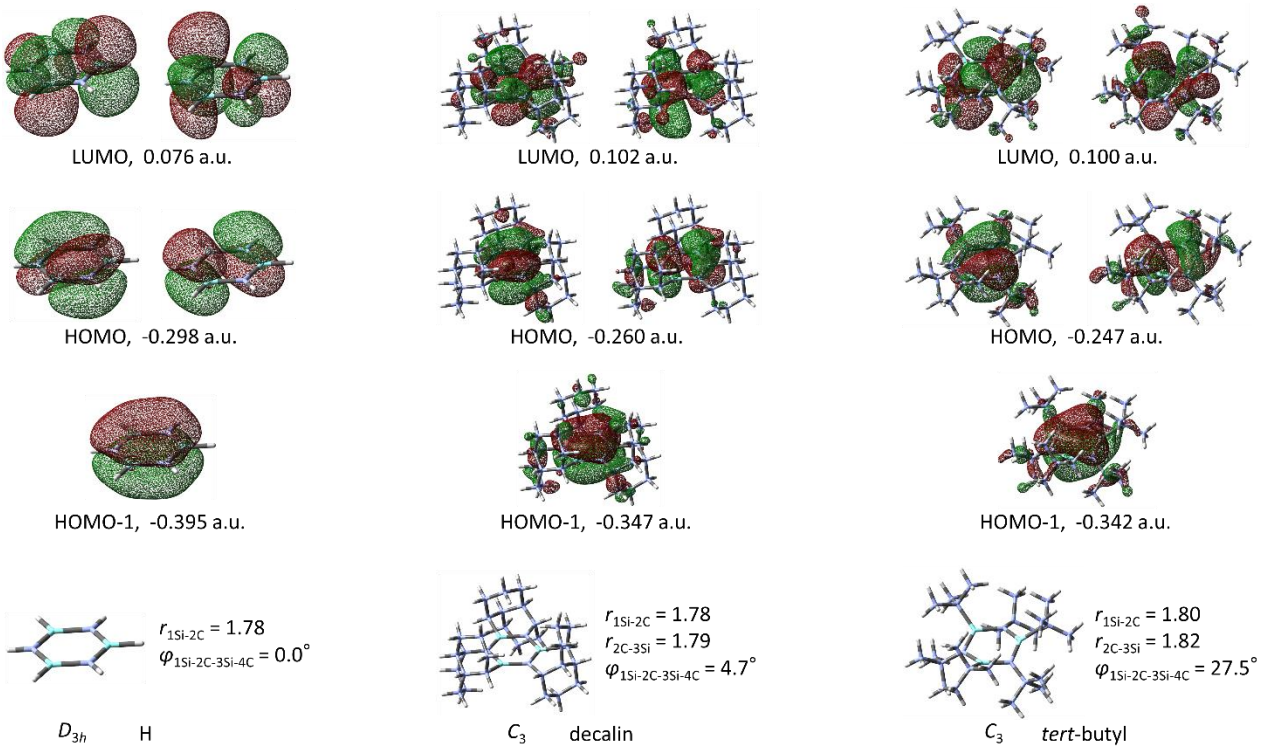

Figure S3. Substituent effects for the 6-membered ring structure (r: bond length, φ: dihedral angle) and the frontier molecular orbitals (MOs) with the energy levels of the trisilabenzenes at the MP2/cc-pVDZ level.