Supporting Information

Table S1 Absolute energies (in au) of SiH_2, BH_3, bridged system $H_2Si\text{-}BH_3$ **1**, isomer $H_3Si\text{-}BH_2$ **1i** and the transition state **1t** for the 1,2-hydrogen shift in $H_2Si\text{-}BH_3$ complex at different theoretical levels.

Level	**SiH_2**	**BH_3**	**$H_2Si\text{-}BH_3$ Bridged system 1**	**$H_3Si\text{-}BH_2$ Isomer 1i**	**$H_2Si\text{-}BH_3$ Transition State 1t**
MP2(Full)/6-31+G*	-290.0801205	-26.4698805	-316.6243881	-316.6317595	-316.6195256
B3LYP/6-31+G*	-290.6150915	-26.6149358	-317.2992848	-317.3076306	-317.2964885
B3PW91/6-31+G*	-290.5599346	-26.5966955	-317.2352963	-317.2406881	-317.2313635
MP4(SDQ)/6-31+G*	-290.0911326	-26.4836783	-316.6428276	-316.6521459	-316.6390910
CCD/6-31+G*	-290.0937060	-26.4838890	-316.6416820	-316.6519935	-316.6381644
CCSD(T)/6-31+G*	-290.0955379	-26.4860604	-316.6511408	-316.6588597	-316.6469067
QCISD(T)/6-31+G*	-290.0955776	-26.4861061	-316.6513557	-316.6589670	-316.6471020
CASSCF[4,6]/6-31+G*	-290.0191188	-26.3909999	-316.4692535	-316.4754061	-316.4637227
CBS-Q	-290.1644262	-26.5224633	-316.7577784	-316.7644317	-316.7562364
G2	-290.1676970	-26.5248150	-316.7620370	-316.7685100	-316.7605540
G3	-290.4575236	-26.5675442	-317.0856359	-317.0946813	-317.0836828

Table S2 Stabilisation energy of **1** due to complexation between H_2Si and BH_3, Si-B-H_b angles in **1**, E between **1** and **1i**, and energy required for 1,2-hydrogen shift in **1** to give **1i** as a function of the variation in the basis set using B3LYP method

Basis Sets	**Stabilisation[@] Energy**	**Si-B-H_b[#]**	**E[@]**	**Barrier for[@] 1,2 H shift**
B3LYP/6-31G*	43.78	58.3	5.53	1.58
B3LYP/6-31+G*	43.46	58.4	5.24	1.75
B3LYP/6-31G**	44.68	58.3	4.90	1.77
B3LYP/6-31++G*	43.36	58.4	5.27	1.72
B3LYP/6-31+G**	44.35	58.4	4.61	1.96
B3LYP/6-31++G**	44.27	58.4	4.64	1.93
B3LYP/6-311+G*	43.91	58.7	4.87	1.73
B3LYP/6-311+G**	44.89	58.6	3.99	2.09
B3LYP/6-311++G*	43.60	58.7	4.88	1.72
B3LYP/6-311++G**	44.85	58.6	4.01	2.08
B3LYP/cc-PVDZ	44.59	58.8	4.11	2.09
B3LYP/cc-PVTZ	45.05	58.7	3.65	2.27

[@]- Energies in kcal/mol.

[#]- angles in degrees

Table S3 Absolute energies (in au) of SiH_2, BH_3, bridged systems $H_2Si\text{-}BH_3$ **1**, isomer $H_3Si\text{-}BH_2$ **1i** and the transition state **1t** for the 1,2-hydrogen shift in $H_2Si\text{-}BH_3$ complex as a function of variation in the basis set at b3LYP method.

Level	**SiH_2**	**BH_3**	**$H_2Si\text{-}BH_3$ Bridged system 1**	**$H_3Si\text{-}BH_2$ Isomer 1i**	**$H_2Si\text{-}BH_3$ Transition State 1t**
B3LYP/6-31G*	-290.6131485	-26.6130002	-317.2959118	-317.3047192	-317.2933969
B3LYP/6-31+G*	-290.6150915	-26.6149358	-317.2992848	-317.3076306	-317.2964885
B3LYP/6-31G**	-290.6152673	-26.6152236	-317.3017891	-317.3096015	-317.2989591
B3LYP/6-31++G*	-290.6152706	-26.6149893	-317.2993611	-317.3077662	-317.2966108
B3LYP/6-31+G**	-290.6172391	-26.6172235	-317.3051410	-317.3124909	-317.3020227
B3LYP/6-31++G**	-290.6174000	-26.6172350	-317.3052071	-317.3160880	-317.3021292
B3LYP/6-311+G*	-290.6370960	-26.6173836	-317.3244535	-317.3322118	-317.3216924
B3LYP/6-311+G**	-290.6404301	-26.6211146	-317.3330856	-317.3394459	-317.3297472
B3LYP/6-311++G*	-290.6372211	-26.6174115	-317.3245346	-317.3323190	-317.3217914
B3LYP/6-311++G**	-290.6405252	-26.6211351	-317.3331406	-317.3953840	-317.3298210
B3LYP/cc-PVDZ	-290.6301402	-26.6095568	-317.3107540	-317.3173130	-317.3077398
B3LYP/cc-PVTZ	-290.6443319	-26.6242175	-317.3403352	-317.3461470	-317.3367165

Table S4 Absolute energies (in au) of SiH_2, BH_3, bridged system $H_2Si\text{-}BH_3$ **1**, isomer $H_3Si\text{-}BH_2$ **1i** and the transition state **1t** for the 1,2-hydrogen shift in $H_2Si\text{-}BH_3$ complex in different solvent calculated using Self Consistent reaction field method (SCRF) at B3LYP/6-31+G* theoretical levels.

Solvent	**Dielectric Constant ( )**	**SiH_2**	**BH_3**	**$H_2Si\text{-}BH_3$ Bridged system 1**	**$H_3Si\text{-}BH_2$ Isomer 1i**	**$H_2Si\text{-}BH_3$ Transition State 1t**
Gas Phase	1.00	-290.6150913	-26.6149360	-317.29922848	-317.3076306	-317.2964885
Heptane	1.92	-290.6151066	-26.6149358	-317.2997420	-317.3076605	-317.2966133
THF	7.58	-290.6151271	-26.6149358	-317.3004495	-317.3077032	-317.2967855
Dichloromethane	8.93	-290.6151285	-26.6149358	-317.3005019	-317.3077063	-317.2967973
Dichloroethane	10.36	-290.6151296	-26.6149358	-317.3005439	-317.3077087	-317.2968067
Ethanol	24.55	-290.6151338	-26.6149358	-317.3007078	-317.3077181	-317.2968426
Acetonitile	36.64	-290.6151349	-26.6149358	-317.3007505	-317.3077205	-317.2968518
DMSO	46.70	-290.6151353	-26.6149358	-317.3007696	-317.3077216	-317.2968559
Water	78.39	-290.6151360	-26.6149358	-317.3007983	-317.3077231	-317.2968620

Table S5 Absolute energies (in au) of the different silylenes and their subsequent bridged structures, isomers and transition states with BH_3 at different theoretical levels.

Structure	Number	HF/6-31+G*	MP2(Full)/6-31+G*	B3LYP/6-31+G*
BH_3		-26.390694	-26.469880	-26.614936
SiH_2		-290.000876	-290.080120	-290.615091
$SiH(CH_3)$		-329.048267	-329.267392	-329.945481
$Si(CH_3)_2$		368.096301	-368.456486	-369.276077
SiHCl		-748.971938	-749.191728	-750.282383
SiHF		-388.940435	-389.205675	-389.940086
SiH(OH)		-364.927500	-365.201366	-365.906289
$SiCl_2$		-1207.944952	-1208.309033	-1209.953592
$SiH(NH_2)$		-345.092526	-345.350734	-346.035050
SiF_2		-487.898385	-488.350620	-489.283192
$Si(OH)_2$		-439.867228	-440.333912	-441.207496
$Si(NH_2)_2$		-400.176558	-400.609564	-401.442284
$(CH\text{-}NH)_2Si$		-475.900702	-476.600381	-477.647452
$(CH_2\text{-}NH)_2Si$		-477.067109	-477.767853	-478.848857
$(CH_2)_2Si$		-366.895315	-367.253758	-368.034885
$(CH_2)_3Si$		-405.937275	-406.431014	-407.353925
$(CH_2)_4Si$		-444.999123	-445.630842	-446.694162
$(CH_2)_5Si$		-484.032778	-484.801084	-486.006857
$(CH_2{=}CH\text{-})HSi$		-366.898535	-367.242346	-368.029528
$(CH_2{=}CH\text{-})_2Si$		-443.796059	-444.405064	-445.443023
(CH C-)HSi		-365.701762	-366.039855	-366.787266
(CH C-)$_2$Si		-441.400840	-442.001428	-442.956452
F(CN)Si		-480.697652	-481.255073	-482.205928
FClSi		-847.921001	-848.329317	-849.617682
F(SH)Si		-786.509089	-786.909772	-788.190519
$(NMe_2)HSi$		-423.143547	-423.678822	-424.649923
Cl(OH)		-823.905360	-824.321048	-825.5796012
F(OH)Si		-463.881195	-464.340413	-465.243884
$SiH_2\text{-}BH_3$	**1**	---[#]	-316.624388	-317.299228
$SiH(CH_3)\text{-}BH_3$	**2**	---[#]	-355.812004	-356.629598
$Si(CH_3)_2\text{-}BH_3$	**3**	---[#]	-395.000186	-395.959555
$SiHCl\text{-}BH_3$	**4**	---[#]	-775.720397	-776.949704
$SiHF\text{-}BH_3$	**5**	-415.363190	-415.733202	-416.609219
$SiH(OH)\text{-}BH_3$	**6**	-391.350798	-391.728866	-392.575148
$SiH(NH_2)\text{-}BH_3$	**7**	-371.511343	-371.873672	-372.699465
$SiCl_2$ BH_3	**8**	-1234.346913	-1234.817963	-1236.600292
SiF_2 BH_3	**9**	-514.295312	-514.849456	-515.926236
$Si(OH)_2\text{-}BH_3$	**10**	-466.276241	-466.843293	-467.859817
$Si(NH_2)_2\text{-}BH_3$	**11**	-426.596529	-427.129829	-428.104328
$(CH\text{-}NH)_2Si$ BH_3	**12**	-502.311086	-503.108695	-504.299351
$(CH_2\text{-}NH)_2Si$ BH_3	**13**	-503.483025	-504.283332	-505.207275
$(CH_2)_2Si$ BH_3	**14**	-393.290688	-393.757242	-394.683545
$(CH_2)_3Si$ BH_3	**15**	-432.366664	-432.955664	-434.023652
$(CH_2)_4Si$ BH_3	**16**	-471.430498	-472.167380	-473.371321

$(CH_2)_5Si$ BH_3	**17**	-510.470327	-511.344728	-512.689768
$(CH_2$=CH-$)HSi$ BH_3	**18**	---[#]	-393.780542	-394.707221
$(CH_2$=CH-$)_2Si$ BH_3	**19**	---[#]	-470.936744	-472.114151
(CH C-)HSi BH_3	**20**	---[#]	-392.516312	-393.462046
(CH C-)$_2$Si BH_3	**21**	---[#]	-468.529043	-469.623899
F(CN)Si BH_3	**22**		-507.769384	-508.861967
FClSi BH_3	**23**	-874.320348	-874.833447	-876.262865
F(SH)Si BH_3	**24**	-812.912499	-813.417836	-814.839722
$(NMe_2)HSi$ BH_3	**25**	-449.562752	-450.201334	-451.314404
Cl(OH)Si BH_3	**26**	-850.310775	-850.830271	-852.229705
F(OH)Si BH_3	**27**	-491.286693	-490.846529	-491.893264
SiH_3-BH_2	**1i**	-316.464420	-316.631759	-317.307631
$SiH_2(CH_3)$ –BH_2	**2i**	-355.510859	-355.816628	-356.635165
$SiH(CH_3)_2$-BH_2	**3i**	-394.551747	-395.002487	-395.962479
SiH_2Cl-BH_2	**4i**	-775.423961	-775.727998	-776.957357
SiH_2F-BH_2	**5i**	-415.393625	-415.740960	-416.616554
$SiH_2(OH)$ –BH_2	**6i**	-391.372267	-391.726934	-392.573529
$SiHCl_2$ - BH_2	**7i**	-1234.382462	-1234.826998	-1236.607994
$SiH(NH_2)$-BH_2	**8i**	-371.526564	-371.865396	-372.691408
$SiHF_2$ – BH_2	**9i**	-514.329494	-514.857212	-515.931687
$SiH(OH)_2$-BH_2	**10i**	-466.290258	-466.834468	-467.850347
$SiH(NH_2)_2$-BH_2	**11i**	-426.595328	-427.108819	-428.083687
$(CH$-$NH)_2Si$ BH_3	**12i**	-502.295904	-503.066554	-504.260305
$(CH_2$-$NH)_2Si$ BH_3	**13i**	-503.476029	-504.253543	-505.477819
$(CH_2)_2SiH$ -BH_2	**14i**	-393.330220	-393.773993	-394.961657
$(CH_2)_3SiH$ - BH_2	**15i**	-432.389585	-432.968434	-434.030388
$(CH_2)_4SiH$ - BH_2	**16i**	-471.451833	-472.168589	-472.001654
$(CH_2)_5SiH$ - BH_2	**17i**	-510.491987	-511.346277	512.691923
SiH_2-BH_3	**1t**	---[#]	-316.619526	-317.296488
$SiH(CH_3)$ -BH_3	**2t**	---[#]	355.805910	-356.625764
$Si(CH_3)_2$-BH_3	**3t**	---[#]	-394.992809	-395.954538
SiHCl-BH_3	**4t**	---[#]	-775.713172	-776.944410
SiHF-BH_3	**5t**	-415.363057	-415.724679	-416.602774
SiH(OH) -BH_3	**6t**	-391.348901	-391.715952	-392.564712
$SiCl_2$ BH_3	**7t**	-1234.346030	-1234.806866	-1236.589836
$SiH(NH_2)$-BH_3	**8t**	-371.5064890	-371.856295	-372.684425
SiF_2 BH_3	**9t**	-514.291059	-514.83297	-515.911524
$Si(OH)_2$-BH_3	**10t**	-466.264035	-466.817721	-467.837166
$Si(NH_2)_2$-BH_3	**11t**	-426.573756	-427.095817	-428.073240
$(CH$-$NH)_2Si$ BH_3	**12t**	-502.278369	-503.057600	-504.253889
$(CH_2$-$NH)_2Si$ BH_3	**13t**	-503.458138	-504.244481	-505.472046
$(CH_2)_2Si$ BH_3	**14t**	-393.298343	-393.753163	-394.679218
$(CH_2)_3Si$ BH_3	**15t**	-432.366033	-432.957021	-434.024133
$(CH_2)_4Si$ BH_3	**16t**	-471.429792	-472.157708	-473.364387
$(CH_2)_5Si$ BH_3	**17t**	-510.470094	-511.336231	-512.683833

[#]**-** These structures could not be located on their respective potential energy surfaces.