Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Cyclopentasilane–borane compound as liquid precursor for p-type semiconducting Si

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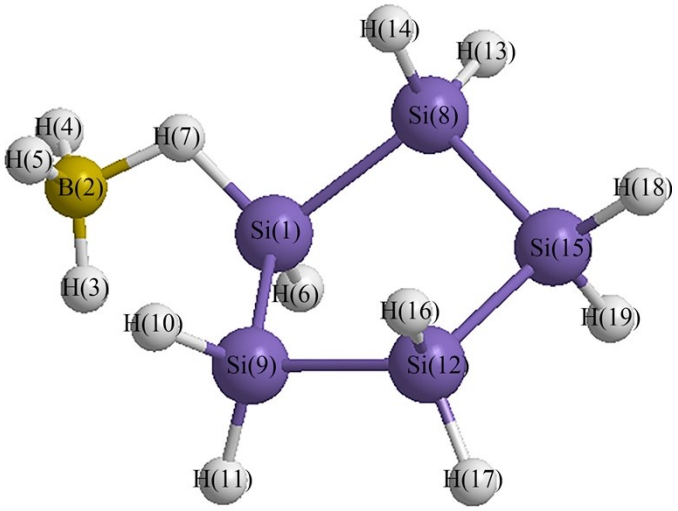
[*]All calculated data were obtained using B3LYP/6-311++G(d,p).

Table S1. NBO charges and bond lengths in RC(P1).

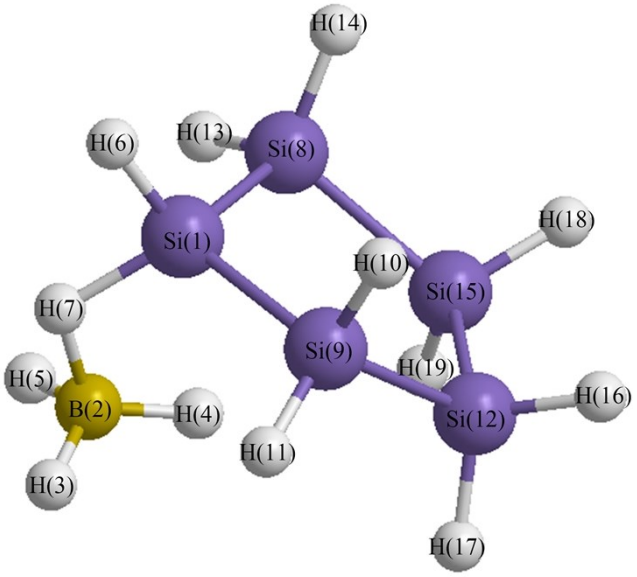
Atom	Number	Natural charge
Si	1	0.42885
B	2	–0.34117
H	3	–0.0122
H	4	0.00266
H	5	–0.01094
H	6	–0.10678
H	7	–0.04767
Si	8	0.23506
Si	9	0.26183
H	10	–0.09979
H	11	–0.10565
Si	12	0.22833
H	13	–0.10493
H	14	–0.11451
Si	15	0.23300
H	16	–0.11265
H	17	–0.10840
H	18	–0.10670
H	19	–0.11832



Bond	Length (angstroms)
Si(1)–H(7)	1.5719
Si(1)–H(6)	1.4820
Si(8)–H(13)	1.4870
Si(8)–H(14)	1.4894
Si(9)–H(10)	1.4854
Si(9)–H(11)	1.4867
Si(12)–H(16)	1.4888
Si(12)–H(17)	1.4877
Si(15)–H(18)	1.4873
Si(15)–H(19)	1.4898
B(2)–H(3)	1.2038
B(2)–H(4)	1.1974
B(2)–H(5)	1.1956
B(2)–H(7)	1.3753
Si(1)–B(2)	2.4173
Si(1)–Si(8)	2.3751
Si(8)–Si(15)	2.3637
Si(15)–Si(12)	2.3690
Si(12)–Si(9)	2.3770
Si(9)–Si(1)	2.3662

Table S2. NBO charges and bond lengths in RC(P2).

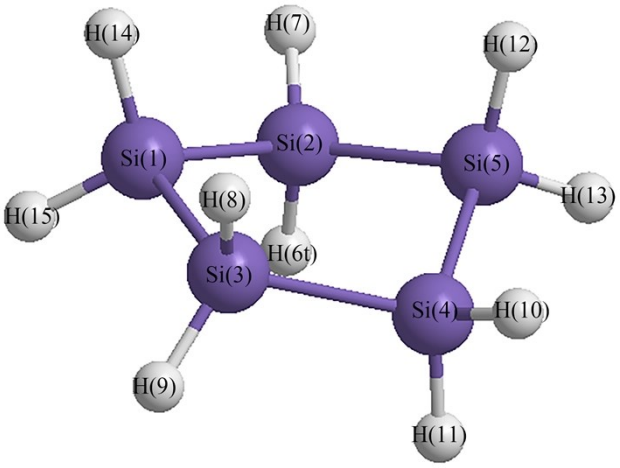
Atom	Number	Natural charge
Si	1	0.43074
B	2	–0.37026
H	3	0.00473
H	4	–0.03113
H	5	0.00467
H	6	–0.11490
H	7	–0.03994
Si	8	0.25638
Si	9	0.25635
H	10	–0.11680
H	11	–0.09957
Si	12	0.23903
H	13	–0.09958
H	14	–0.11683
Si	15	0.23905
H	16	–0.11338
H	17	–0.10761
H	18	–0.11334
H	19	–0.10761



Bond	Length (angstroms)
Si(1)–H(7)	1.5890
Si(1)–H(6)	1.4929
Si(8)–H(13)	1.4854
Si(8)–H(14)	1.4900
Si(9)–H(10)	1.4900
Si(9)–H(11)	1.4854
Si(12)–H(16)	1.4888
Si(12)–H(17)	1.4866
Si(15)–H(18)	1.4887
Si(15)–H(19)	1.4866
B(2)–H(3)	1.1960
B(2)–H(4)	1.2092
B(2)–H(5)	1.1960
B(2)–H(7)	1.3481
Si(1)–B(2)	2.3947
Si(1)–Si(8)	2.3572
Si(8)–Si(15)	2.3705
Si(15)–Si(12)	2.3787
Si(12)–Si(9)	2.3707
Si(9)–Si(1)	2.3572

Table S3. NBO charges and bond lengths in CPS. The average NBO charges for Si and H are 0.2302 and –0.1151, respectively, and the average bond length for Si–H and Si–Si are 1.489 and 2.369, respectively.

Atom	Number	Natural charge
Si	1	0.22985
Si	2	0.23021
Si	3	0.22994
Si	4	0.22995
Si	5	0.23112
H	6	–0.11979
H	7	–0.11111
H	8	–0.11569
H	9	–0.11305
H	10	–0.11125
H	11	–0.11918
H	12	–0.12118
H	13	–0.11091
H	14	–0.11639
H	15	–0.11251



Bond	Length (angstroms)
Si(1)–H(14)	1.4895
Si(1)–H(15)	1.4886
Si(2)–H(6)	1.4902
Si(2)–H(7)	1.4881
Si(3)–H(8)	1.4893
Si(3)–H(9)	1.4887
Si(4)–H(10)	1.4882
Si(4)–H(11)	1.4901
Si(5)–H(12)	1.4903
Si(5)–H(13)	1.4880
Si(1)–Si(2)	2.3694
Si(2)–Si(5)	2.3633
Si(5)–Si(4)	2.3638
Si(4)–Si(3)	2.3715
Si(3)–Si(1)	2.3778

Table S4. Sum of electronic and thermal Enthalpies (unit: Hartree) of CPS, BH_3, and H_2.

Compound	
CPS	–1453.525248
BH_3	–26.591173
H_2	–1.166202

Table S5. Sum of electronic and thermal Enthalpies (unit: Hartree) of each compounds.

Pathway	Compounds				
	RC	TS1	IC	TS2	FP (without H_2)
P1	–1480.121372	–1480.108772	–1480.109223	–1480.106228	–1478.941673
P2	–1480.123010	–1480.110349	–1480.110229	–1480.064642	–1478.933466
P3	–2932.469268	–2932.460848	–2932.459539	–2932.454111	–2931.294459
P4	–2932.475394	–2932.459120	–2932.458058	–2932.452559	–2931.294466
P5	–2932.475386	–2932.417862			–2931.297712

Cartesian Coordinates of RC structures

RC(P1)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.724918	1.480308	-0.271429
B	-2.237213	2.504926	-1.854539
H	-1.129849	2.825419	-2.201213
H	-2.896038	3.405771	-1.420614
H	-2.75907	1.659369	-2.519534
H	-0.024867	2.717579	0.147256
H	-2.20863	1.825522	-0.659071
Si	-1.159379	0.145087	1.644193
Si	0.534517	0.107488	-1.730187
H	-0.362004	-0.450479	-2.774879
H	1.593726	0.924363	-2.379156
Si	1.432089	-1.621518	-0.368125
H	-1.521662	0.941665	2.846471
H	-2.270271	-0.797951	1.336232
Si	0.858005	-1.067245	1.862383
H	0.786807	-2.910042	-0.741951
H	2.901572	-1.76123	-0.553773
H	0.743211	-2.258396	2.74559
H	1.900382	-0.161671	2.421783

RC(P2)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	0.923299	1.125514	1.427163
B	-0.35473	-0.307637	2.858053
H	0.303939	-1.095613	3.470993
H	-0.583003	-0.652949	1.721916
H	-1.281463	0.233895	3.38562
H	1.810245	2.21553	1.931078
H	0.509592	0.725668	2.908299
Si	-0.850433	1.897442	0.080173
Si	2.072051	-0.552525	0.235121
H	3.138583	0.107442	-0.569324
H	2.70222	-1.540004	1.148502
Si	0.423211	-1.488874	-1.187833
H	-1.986044	2.392888	0.899569
H	-0.335121	3.018461	-0.755255
Si	-1.399877	0.0362	-1.28121
H	0.991924	-1.699516	-2.547464
H	-0.027584	-2.804307	-0.662071
H	-1.62782	0.485502	-2.682114
H	-2.644266	-0.613059	-0.791372

RC(P3)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	0.580613	0.581842	-1.253523
B	0.358707	0.647709	0.763019
H	1.380452	0.998261	1.293363
H	-0.619952	1.175029	1.209369
H	-0.569187	-0.02259	-1.998404
Si	0.804993	2.778797	-2.120425
Si	2.519997	-0.552204	-2.040056
H	-0.506219	3.461912	-2.304567
H	1.624123	3.610338	-1.192122
Si	1.998408	2.514983	-4.142486
H	2.149513	-1.836826	-2.701054
Si	3.608126	0.872861	-3.596261
H	3.445443	-0.889287	-0.919649
Si	-0.558959	-1.610091	1.124769
H	0.542575	-0.520274	1.428929
Si	-2.792854	-0.930352	0.801606
Si	-0.560826	-2.54251	3.306357
Si	-3.49533	-0.174006	2.936577
H	-2.954831	0.056554	-0.291855
H	-3.540231	-2.174197	0.458499
H	-1.182026	-3.893072	3.207825
H	0.805527	-2.677779	3.87548
Si	-1.976641	-1.085823	4.521959
H	0.068546	-2.45869	0.083004
H	-4.882143	-0.644831	3.200459
H	-3.481163	1.311146	2.995512
H	-2.685495	-1.806991	5.612992
H	-1.162323	0.003346	5.124816
H	4.767336	1.534009	-2.931671
H	4.122138	0.13828	-4.785564
H	1.082254	1.975819	-5.187955
H	2.599605	3.77512	-4.66084

RC(P4, P5)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	0.362196	0.954716	-1.860905
B	-0.720849	0.724806	-0.138201
H	-0.012995	0.998868	0.789034
H	-1.768693	1.28805	-0.283688
H	-0.399277	0.470551	-3.053385
Si	0.920326	3.216791	-2.276897
Si	2.483565	-0.090029	-1.953683
H	-0.242405	4.035498	-2.719264
H	1.460267	3.824304	-1.027122
Si	2.644794	3.14652	-3.903561
H	2.413664	-1.567973	-2.133971

Si	3.613868	0.982259	-3.737901
H	3.221648	0.175335	-0.685075
Si	-1.692339	-0.84303	1.019613
H	-0.756677	-0.499544	-0.410629
Si	-2.66676	0.258517	2.87056
Si	-0.353545	-2.528691	1.999036
Si	-3.080368	-1.487686	4.425495
H	-1.669713	1.209486	3.430235
H	-3.891426	1.008118	2.48468
H	0.049009	-3.594089	1.042332
H	0.87309	-1.902187	2.564122
Si	-1.723061	-3.324566	3.759763
H	-2.770411	-1.49977	0.226589
H	-4.516527	-1.877701	4.396961
H	-2.744266	-1.04397	5.805902
H	-2.594489	-4.418581	3.249046
H	-0.918846	-3.858159	4.892147
H	5.084485	1.049554	-3.512296
H	3.380346	0.234212	-5.005144
H	2.075274	3.339635	-5.266567
H	3.657116	4.21541	-3.676841

Cartesian Coordinates of TS structures

TS1(P1)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	1.730858	-3.083191	-0.961365
B	0.242121	-1.931551	-1.889389
H	0.774328	-1.549629	-2.882537
H	-0.161144	-1.245765	-1.004784
H	-0.801729	-2.502102	-2.317071
H	2.741804	-2.040811	-0.625788
H	-0.067412	-3.139927	-1.848043
Si	1.182469	-4.234451	1.031647
Si	2.810297	-4.761463	-2.232564
H	1.770039	-5.659762	-2.813692
H	3.629641	-4.223549	-3.352398
Si	4.08896	-5.988131	-0.659291
H	0.879463	-3.33094	2.174705
H	-0.023955	-5.07515	0.777545
Si	3.032715	-5.656539	1.444962
H	4.16202	-7.431504	-1.016549
H	5.478412	-5.454248	-0.610529
H	2.606391	-6.946251	2.054267
H	3.981722	-4.995037	2.382874

TS2(P1)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.641835	1.347439	-0.559971
B	-2.04382	2.054854	-1.81059
H	-2.909471	1.326369	-2.183469
H	-1.907564	3.105979	-2.351966
H	-3.705665	2.953433	-0.734152
H	0.242926	2.393102	0.035358
H	-3.177307	2.980076	-0.200995
Si	-1.3342	-0.10459	1.175206
Si	0.772665	-0.099605	-1.808481
H	-0.072313	-1.032296	-2.607127
H	1.66755	0.62784	-2.749762
Si	1.969793	-1.336946	-0.179145
H	-1.905451	0.61894	2.345493
H	-2.386758	-1.017692	0.645455
Si	0.580451	-1.379611	1.745887
H	2.300609	-2.706754	-0.660079
H	3.246595	-0.637935	0.136477
H	0.220938	-2.771561	2.133451
H	1.291048	-0.751268	2.89414

TS1(P2)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	-0.012214	-0.062937	0.006371
B	0.035617	-0.202636	2.090995
H	1.187443	-0.336427	2.358355
H	-0.831735	-0.974858	2.351598
H	-0.295911	0.813952	2.77791
H	0.940139	0.962242	-0.516062
H	-0.32433	0.938352	1.721403
Si	-2.08885	0.312179	-1.06339
Si	0.64446	-2.159106	-0.869663
H	2.104921	-2.404032	-0.724132
H	-0.088338	-3.23195	-0.141962
Si	-0.059976	-2.120273	-3.134586
H	-3.13444	-0.52639	-0.411631
H	-2.53669	1.731846	-1.007058
Si	-1.743946	-0.448408	-3.27943
H	1.081637	-1.767695	-4.023439
H	-0.578753	-3.450434	-3.55701
H	-1.251967	0.677382	-4.121622
H	-2.99455	-0.971723	-3.894365

TS2(P2)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	1.361262	-3.497075	-1.132185
B	0.112104	-2.12576	-2.129356
H	0.680161	-1.875709	-3.157025
H	-0.072736	-1.233264	-1.348493
H	-0.937685	-2.725639	-2.353571
H	0.181757	-4.673255	-1.239953
H	-0.156641	-3.852216	-1.655613
Si	1.550848	-3.755864	1.216398
Si	3.001238	-4.871998	-2.166384
H	2.341628	-5.852733	-3.069413
H	3.920961	-4.025666	-2.971645
Si	4.133318	-5.939484	-0.376453
H	2.392952	-2.63625	1.719753
H	0.220063	-3.695303	1.875671
Si	2.666426	-5.821983	1.477789
H	4.52141	-7.336364	-0.709915
H	5.369496	-5.167764	-0.068189
H	1.655551	-6.910749	1.368708
H	3.372823	-5.957718	2.780153

TS1(P3)

Atom	Coordinates (Angstroms)		
	X	Y	Z

Si	0.009663	-0.001647	0.005413
B	0.004624	-0.000046	2.035459
H	1.262766	-0.000752	2.211811
H	-0.36051	0.933569	2.681983
H	-1.367922	-0.257006	-0.516119
Si	0.713889	2.027242	-0.99194
Si	1.409816	-1.635822	-1.003619
H	-0.299338	3.114298	-0.897566
H	1.96069	2.501917	-0.323701
Si	1.227769	1.422939	-3.217409
H	0.661867	-2.889266	-1.299366
Si	2.298109	-0.675864	-2.988577
H	2.526564	-1.993884	-0.080029
Si	-1.127177	-1.626045	2.659359
H	0.756694	-0.762483	2.699289
Si	-3.414306	-1.151166	2.207973
Si	-1.073688	-2.182128	4.965236
Si	-4.654756	-1.957171	4.066963
H	-3.613058	0.313763	2.03956
H	-3.837261	-1.828831	0.952539
H	0.109172	-3.011973	5.327705
H	-1.02454	-0.932088	5.776163
Si	-3.140989	-3.263428	5.330421
H	-0.752834	-2.86267	1.911904
H	-5.860853	-2.719894	3.644186
H	-5.102046	-0.798564	4.889708
H	-3.076294	-4.637882	4.75896
H	-3.516507	-3.3687	6.766462
H	3.764819	-0.4713	-2.82175
H	2.090018	-1.553841	-4.172909
H	-0.040458	1.243892	-3.979577
H	2.065436	2.420393	-3.93854

TS2(P3)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	1.331217	-0.073727	-1.313182
B	1.010271	-0.155932	0.679094
H	2.493038	-1.368795	0.872276
H	1.571828	0.649375	1.35457
H	0.702915	-1.202518	-2.063323
Si	0.399671	1.926542	-2.189085
Si	3.567041	0.117961	-2.072431
H	-1.088175	1.91583	-2.22173
H	0.833131	3.072976	-1.340907
Si	1.35358	2.155407	-4.347429
H	4.313933	-1.170287	-2.009655
Si	3.417126	0.982348	-4.272853
H	4.285353	1.098929	-1.209122

Si	-0.670487	-0.981927	1.435457
H	2.056627	-1.569664	1.460609
Si	-2.364815	0.672879	1.600974
Si	-0.61427	-1.774014	3.667273
Si	-4.01057	-0.266603	3.026347
H	-1.793041	1.886248	2.250836
H	-2.919498	1.077382	0.280532
H	0.087819	-3.081744	3.80237
H	0.111701	-0.782043	4.511371
Si	-2.877729	-1.874243	4.357493
H	-1.225848	-2.080206	0.58872
H	-5.061042	-0.93633	2.210195
H	-4.669817	0.775999	3.860301
H	-3.429965	-3.2307	4.086838
H	-3.028896	-1.596406	5.812366
H	4.569308	1.866505	-4.600738
H	3.398081	-0.134956	-5.257416
H	0.456895	1.533786	-5.361206
H	1.542379	3.586053	-4.714396

TS1(P4)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	0.735059	0.698853	-1.196796
B	-0.106418	1.206666	0.580399
H	0.924637	1.628675	1.165
H	-0.890555	2.099833	0.68405
H	-0.076039	-0.32951	-1.917925
Si	0.955351	2.526916	-2.683794
Si	2.956617	-0.121312	-1.143593
H	-0.344783	3.011951	-3.224158
H	1.60416	3.66127	-1.964706
Si	2.416991	1.763762	-4.38389
H	3.0714	-1.516528	-0.63531
Si	3.771342	0.102069	-3.359004
H	3.766268	0.750214	-0.241574
Si	-1.133811	-0.468082	1.271288
H	0.371833	0.871462	1.688293
Si	-2.196678	-0.268172	3.379611
Si	0.009408	-2.530358	1.48738
Si	-2.923339	-2.460751	3.901445
H	-1.17895	0.156832	4.385009
H	-3.299291	0.731318	3.391822
H	0.418248	-3.128158	0.188695
H	1.238454	-2.302586	2.301228
Si	-1.474688	-3.919076	2.707796
H	-2.205832	-0.631642	0.248687
H	-4.32357	-2.65461	3.433124
H	-2.884375	-2.722858	5.366219

H	-2.266855	-4.760631	1.768861
H	-0.730574	-4.825118	3.625111
H	5.211501	0.481199	-3.370382
H	3.632715	-1.19043	-4.086281
H	1.632061	1.149111	-5.490892
H	3.237515	2.864781	-4.960225

TS2(P4)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	1.200667	0.698984	-0.993854
B	0.282987	0.968516	0.779745
H	1.717993	-0.025105	1.751006
H	0.458698	2.030042	1.296141
H	1.113652	-0.696928	-1.518716
Si	0.122957	2.090878	-2.588907
Si	3.446574	1.416242	-1.209351
H	-1.230103	1.602137	-2.970063
H	-0.025305	3.458008	-2.013973
Si	1.616592	2.176329	-4.42764
H	4.421071	0.443969	-0.639512
Si	3.779226	1.787719	-3.526569
H	3.608618	2.70522	-0.47806
Si	-1.308908	-0.153213	1.350497
H	1.499495	0.445756	2.300798
Si	-2.17939	0.187595	3.526269
Si	-1.034865	-2.509306	1.223802
Si	-3.625548	-1.650258	3.861144
H	-1.064899	0.113266	4.516482
H	-2.851144	1.505729	3.694201
H	-1.303644	-3.026077	-0.146318
H	0.370036	-2.871	1.572195
Si	-2.507409	-3.465594	2.826412
H	-2.409717	0.188843	0.395296
H	-4.905603	-1.392556	3.142924
H	-3.941142	-1.914666	5.291831
H	-3.464589	-4.414784	2.194251
H	-1.717792	-4.218626	3.840972
H	4.692304	2.937716	-3.772838
H	4.379235	0.579158	-4.156806
H	1.275087	1.097523	-5.396012
H	1.537104	3.480285	-5.141952

TS(P5)

Atom	Coordinates (Angstroms)		
	X	Y	Z
Si	0.094173	-0.10123	-0.062522
B	0.222838	-0.148828	1.987019

H	1.376716	-0.254035	2.310906
H	-0.342298	0.838018	2.379209
H	0.468539	-1.400833	-0.726338
Si	-1.993881	0.447657	-1.039516
Si	1.518145	1.514983	-1.041819
H	-2.98549	-0.666542	-0.992845
H	-2.600855	1.606234	-0.321705
Si	-1.514548	1.09406	-3.269647
H	2.960107	1.149872	-0.961422
Si	0.774576	1.733041	-3.280949
H	1.337217	2.81984	-0.343636
Si	-0.710125	-1.691723	3.013772
H	-0.246871	-1.842986	1.470125
Si	-3.050719	-2.01927	3.198207
Si	0.404457	-3.108587	4.56327
Si	-3.219375	-4.146132	4.214154
H	-3.572269	-0.958624	4.102291
H	-3.721281	-1.915484	1.877223
H	1.315628	-4.024259	3.827657
H	1.203177	-2.278461	5.502183
Si	-1.347798	-4.271562	5.659395
H	-0.566611	-2.752102	1.74109
H	1.542089	0.809206	-4.163508
H	0.956659	3.115484	-3.806103
H	-2.395736	2.203868	-3.730116
H	-1.719594	-0.057278	-4.193731
H	-3.08485	-5.18035	3.151049
H	-4.506525	-4.357742	4.928633
H	-0.969731	-5.672255	5.986867
H	-1.662763	-3.555982	6.926809

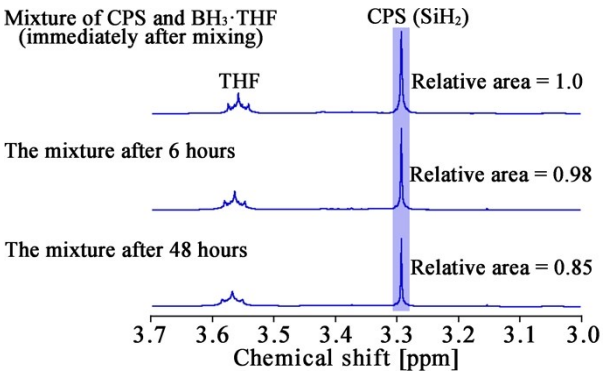


Fig. S1 ^{1}H NMR spectrum of the mixture of CPS and BH_3·THF. The three samples are the same, except for the time. A closed NMR tube was employed to prevent sample evaporation. Relative area of CPS peak is shown in the figure (highlighted in blue). Almost no change was observed in the CPS peak at 3.29 ppm in the 6 h sample, indicating no dehydrogenation. The decreasing peak for the 48 h sample indicates dehydrogenation.

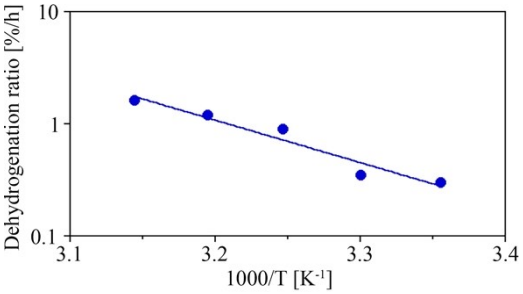


Fig. S2 Arrhenius plot for dehydrogenation ratio for 1 h. Since the boiling point of THF, which is the main component of BH_3THF, is as low as 66 °C, the measurements were conducted in a lower and limited temperature range. Therefore, the quantitativeness is insufficient. The slope of the plot representing the activation energy is 17 kcal·mol^{-1}, and the T^{-1} = 0 intercept representing the rate constant is 1.4 × 10^{12} mol% H_2·h^{-1}.

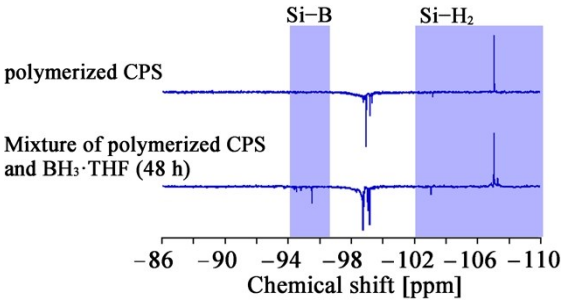


Fig. S3 ^{29}Si NMR spectrum of polymerized CPS and the mixture (polymerized CPS + BH_3·THF). The mixture was kept at 25 °C 48 h before measurement. The growth of a peak near –96 ppm indicates that the reaction will form a Si–B bond between the polymerized CPS and BH_3 proceeded.