Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Directed Gas-Phase Preparation of the Elusive Phosphinosilylidyne ($SiPH_2$, X^2A'') and Cis/Trans Phosphinidenesilyl (HSiPH; X^2A') Radicals Under Single-Collision Conditions

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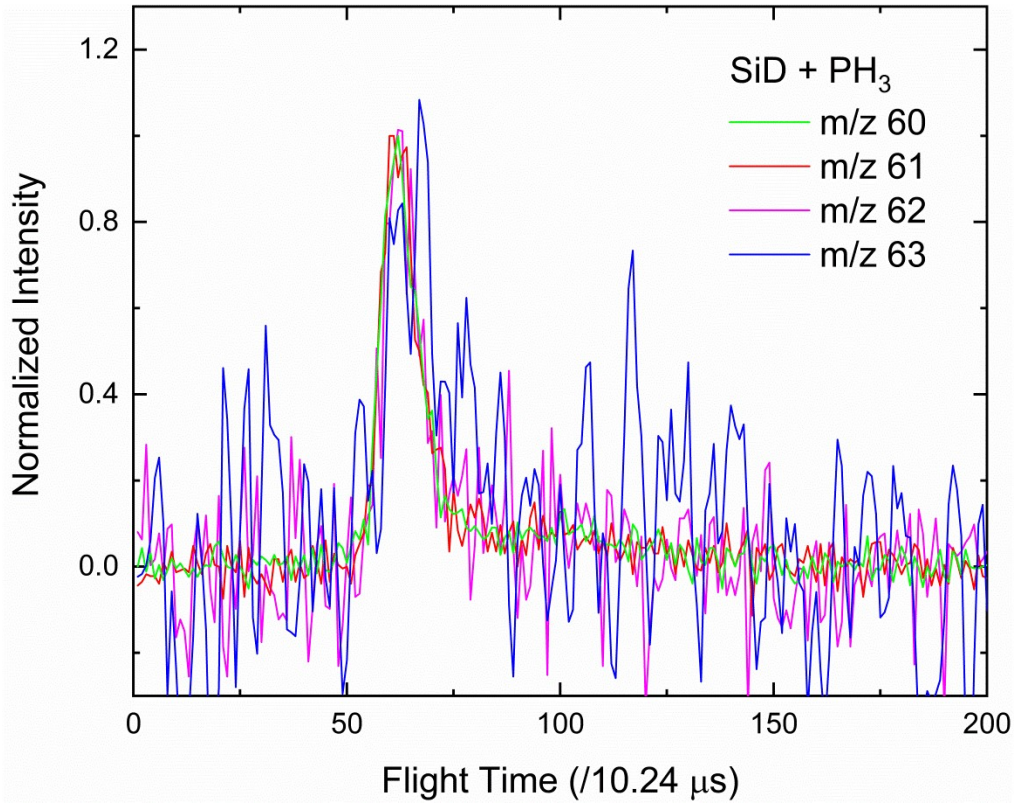

Figure S1. TOF spectra collected at m/z = 60, 61, 62, and 63 for the reaction of the D1-silylidyne radical (SiD; $X^2\Pi$) with phosphine (PH_3; X^1A_1) at center-of-mass (CM) angle of 36°.

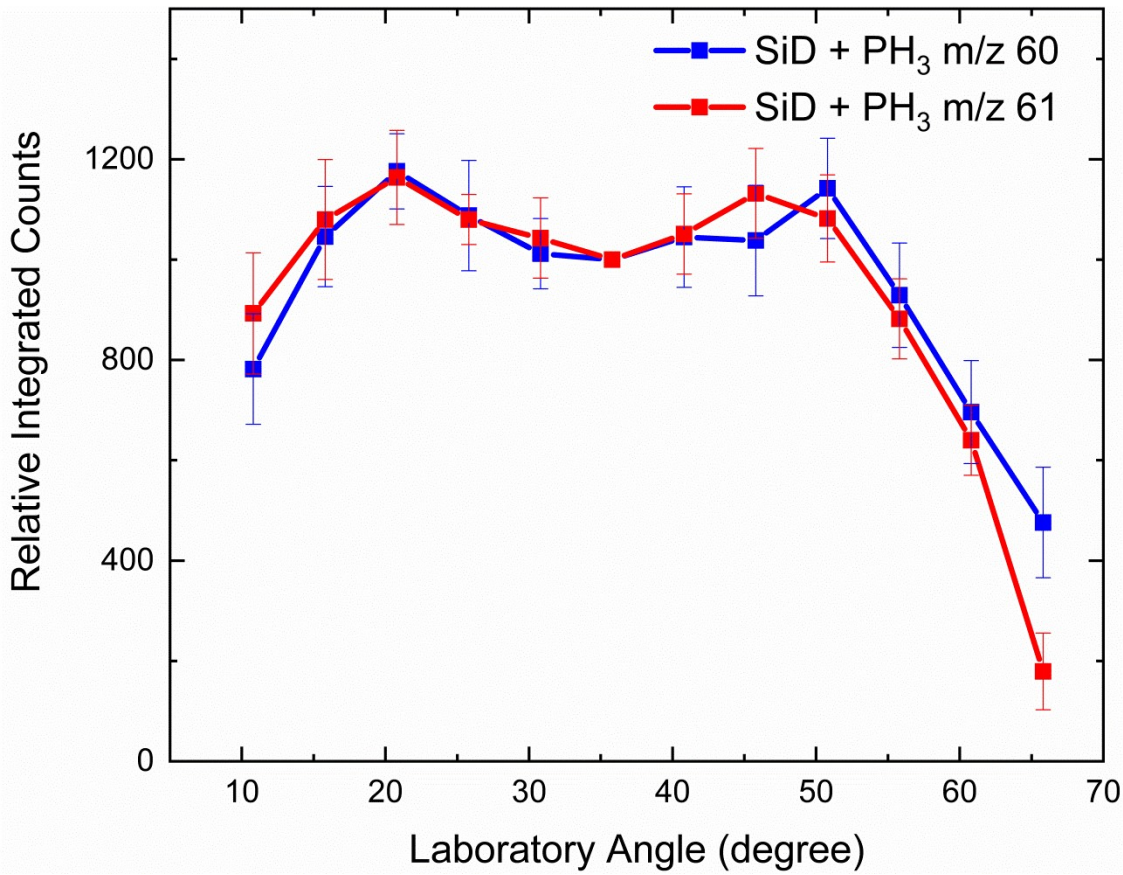

Figure S2. Laboratory angular distribution recorded at m/z = 60 and m/z = 61 for the reaction of the D1-silylidyne radical (SiD; $X^2\Pi$) with phosphine (PH_3; X^1A_1).

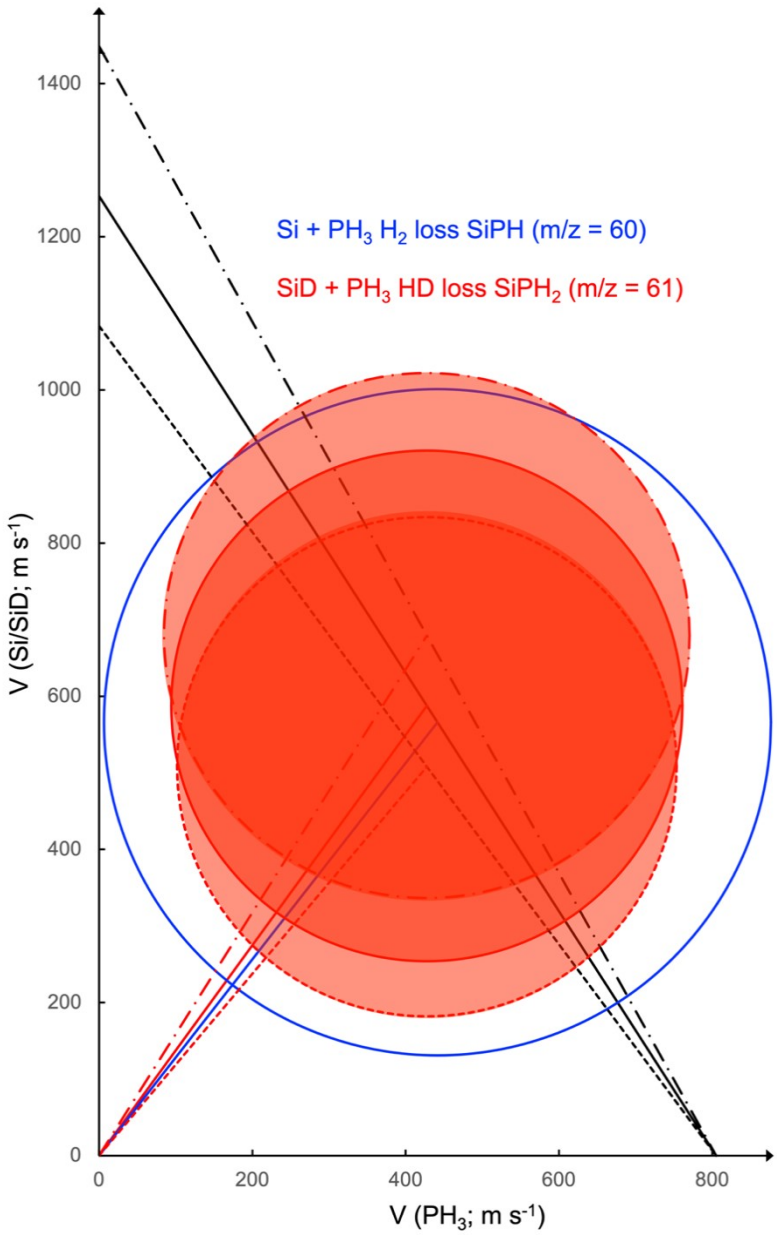

Figure S3. Newton diagram for the reaction of ground state atomic silicon (Si; ^{3}P) with phosphine (PH_3) and of the D1-silylidyne radical (SiD; $X^2\Pi$) with phosphine (PH_3). The diagram is simplified by including only the most energetically favorable product channels for the H_2 loss pathway for the reaction of the ground state atomic silicon (Si; ^{3}P) with phosphine (PH_3), and HD loss pathway for the reaction of the D1-silylidyne radical (SiD; $X^2\Pi$) with phosphine (PH_3). Each Newton circle has a radius equal to the maximum CM recoil velocity of its corresponding heavy product. Due to the lower speed ratio of the SiD beam, Newton diagrams and recoil circles were also added for the velocity at the FWHM (full width at half maximum) values.

Table S1. The relative signal ratios between the m/z = 65, 64, 63, 62, 61, and 60 for the reaction of ground state atomic silicon (Si; ^3P) with phosphine (PH_3), and for the reaction of the D1-silylidyne radical (SiD; $X^2\Pi$) with phosphine (PH_3), respectively.

	Si + PH_3 reaction	SiD + PH_3 reaction
m/z = 65	No signal	No signal
m/z = 64	No signal	No signal
m/z = 63	No signal	0.04 ± 0.01
m/z = 62	0.03 ± 0.03	0.09 ± 0.01
m/z = 61	0.07 ± 0.03	1
m/z = 60	1	1.10 ± 0.01

Table S2. The H, D, HD, and H_2 loss products from the D1-silylidyne radical (SiD; $X^2\Pi$) plus phosphine (PH_3; X^1A_1) reaction considering isotopes of silicon.

SiD + PH_3	PH_3 (m/z 34)			
	H loss	D loss	HD loss	H_2 loss
^{28}SiD (92.2%)	$^{28}SiPDH_2$ (m/z 63)	$^{28}SiPH_3$ (m/z 62)	$^{28}SiPH_2$ (m/z 61)	^{28}SiPDH (m/z 62)
^{29}SiD (4.7%)	$^{29}SiPDH_2$ (m/z 64)	$^{29}SiPH_3$ (m/z 63)	$^{29}SiPH_2$ (m/z 62)	^{29}SiPDH (m/z 63)
^{30}SiD (3.1%)	$^{30}SiPDH_2$ (m/z 65)	$^{30}SiPH_3$ (m/z 64)	$^{30}SiPH_2$ (m/z 63)	^{30}SiPDH (m/z 64)

Table S3. The H, and H_2 loss products from the silicon atom (Si; ^3P) plus phosphine (PH_3; X^1A_1) reaction considering isotopes of silicon.

Si + PH_3	PH_3 (m/z 34)	
	H loss	H_2 loss
^{28}Si (92.2%)	$^{28}SiPH_2$ (m/z 61)	$^{28}SiPH$ (m/z 60)
^{29}Si (4.7%)	$^{29}SiPH_2$ (m/z 62)	$^{29}SiPH$ (m/z 61)
^{30}Si (3.1%)	$^{30}SiPH_2$ (m/z 63)	$^{30}SiPH$ (m/z 62)

Table S4. Statistical branching ratios (%) for the reaction of the D1-silylidyne radical (SiD; $X^2\Pi$) with phosphine (PH_3; X^1A_1).

E_C (kJ mol^{-1})	**p1'**	**p1**	**p2'**	**p2**	**p3**	**p4'**	**p4**
17.7	0	0	15.76	15.76	21.71	15.59	31.19

Table S5. Rate constant (k, in s^{-1}) for all unimolecular reactions in the SiD + PH_3 system calculated using RRKM theory at E_C = 17.7 kJ mol^{-1}.

Reaction	k	Reaction	k	Reaction	k	Reaction	k
i0 → i2a	1.26E+11	**i1 → i2b**	5.85E+10	**i2a → i2b**	3.41E+12	**i2a → i3**	8.45E+10
i2a → i0	3.12E+07	**i2b → i1**	8.02E+08	**i2b → i2a**	3.50E+12	**i3 → i2a**	3.16E+10
i2b → p2	2.31E+07	**i3 → p4**	1.25E+07	**i2a → p3**	3.09E+07		
i2b → p2'	2.31E+07	**i3 → p4'**	1.25E+07				

Table S6. Optimized Cartesian coordinates (Å) and vibrational frequencies (cm^{-1}) for all species involved in the SiD/SiH + PH_3 reaction. The energies are given relative to the reactants at the CCSD(T)-F12/cc-pVQZ-F12//M06-2X/cc-pV(T+d)Z+ZPE(M06-2X/cc-pV(T+d)Z) level in kJ mol^{-1}. To account for the different ZPE among the possible isotopologues, we employ the following notation:

E(D0) – relative energy of the non-deuterated case
E(D1) – relative energy for one deuterium at the first position of the Cartesian coordinates
E(D2) – relative energy for one deuterium at the second position of the Cartesian coordinates
E(D3) – relative energy for one deuterium at the third position of the Cartesian coordinates
E(D4) – relative energy for one deuterium at the fourth position of the Cartesian coordinates

REACTANTS

SiH

H	0.0000000000	0.0000000000	-0.7578444535
Si	0.0000000000	0.0000000000	0.7578444535

Frequencies

2080.464

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01333901

PH_3

H	-0.6826536606	-1.0274842429	-0.6156233055
H	-0.6826538144	1.0274840772	-0.6156228017
H	-0.7320439127	0.0000003515	1.1624302654
P	0.0657489556	-0.0000001858	-0.0019137497

Frequencies

1020.828
1156.119
1156.576
2457.598
2460.576
2462.354

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01409732

PRODUCTS

H_2

H	0.0000000000	0.0000000000	0.3694968462
H	0.0000000000	0.0000000000	-0.3694968462

Frequencies

4464.920

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.00589562

p1: H_2SiP

H	-0.0001887201	1.2189960445	-1.8473287573
H	-0.0001887572	-1.2189951724	-1.8473215647
Si	-0.0000453118	0.0000032107	-1.0164390575
P	0.0003089458	-0.0000040339	1.0340789607

Frequencies

470.927
532.046
637.480
951.198
2270.951
2289.755

E(p1-D0 + H_2) = -87.2
E(p1-D0 + HD) = -87.3
E(p1-D1 + H_2) = -89.1
E(p1-D2 + H_2) = -89.1

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01893614

p2: t-HSiPH

H	0.0000540530	-1.2015483824	-1.8455445284
H	-0.0004326876	1.3367092419	1.1678999845
Si	-0.0011210638	0.0596564339	-1.0510345662
P	0.0015509974	-0.0698774999	1.0066789432

Frequencies

486.108
517.489
618.941
799.884
2184.361
2425.324

E(p2-D0 + H_2) = -67.2
E(p2-D0 + HD) = -67.3
E(p2-D1 + H_2) = -68.8
E(p2-D2 + H_2) = -69.3

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02884715

p3: $SiPH_2$

H	0.6119847560	1.0883458853	-1.5867559586
H	0.6119848955	-1.0883461746	-1.5867583718
P	-0.0070832451	-0.0000007651	-0.9524594477
Si	-0.0070268171	0.0000010829	1.2061086167

Frequencies

85.664
516.442
519.684
1099.794
2476.686
2489.275

E(p3-D0 + H_2) = -54.5
E(p3-D0 + HD) = -54.6
E(p3-D1 + H_2) = -56.6
E(p3-D2 + H_2) = -56.6

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02185492

p4:c-HSiPH

H	0.0001236412	-1.3900810571	0.8534957485
H	0.0003978713	-1.1644669015	-1.9165046913
Si	-0.0002891442	0.0599311195	-1.0656052695
P	-0.0002405733	0.0247875833	1.0033437233

Frequencies

443.110
496.689
620.344
728.547
2172.667
2384.890

E(p4-D0 + H_2) = -52.8
E(p4-D0 + HD) = -52.9
E(p4-D1 + H_2) = -54.6
E(p4-D2 + H_2) = -54.4

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02262111

p5: H_2SiPH

H	-0.0011869734	1.2238955015	-1.8522254331
H	0.0008003725	-1.2083840326	-1.8778493892
H	0.0001479545	-1.3725789235	1.0204239941
Si	-0.0004061624	-0.0006313767	-1.0335912507
P	-0.0011280030	0.0447444991	1.0224291721

Frequencies

471.271
540.246
619.442
630.834
758.777
972.929
2284.226
2307.183
2420.222

E(p5-D0 + H or D) = 12.3
E(p5-D1 + H) = 10.1
E(p5-D2 + H) = 10.2

E(p5-D3 + H) = 10.1

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01766472

p6: $HSiPH_2$

H	0.6157392084	1.1297506545	-1.4984142360
H	0.7609067573	-1.0236709519	-1.5202845471
H	-0.0376407214	-1.4595427092	1.1860358819
P	-0.0611302598	-0.0022466922	-1.0210012220
Si	0.0230950033	0.0508314562	1.1814841787

Frequencies

209.076
488.062
513.009
519.667
818.151
1107.689
2099.036
2491.272
2510.576

E(p6-D0 + H or D) = 70.3
E(p6-D1 + H) = 67.6
E(p6-D2 + H) = 67.9
E(p6-D3 + H) = 68.6

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02047507

INTERMEDIATES

i1: $HSiPH_3$

H	0.3346158710	1.3071373910	1.2873276285
H	-0.5110681246	-1.0680994100	-1.6464747752
H	-0.7511826435	1.0496812958	-1.6466848718
H	1.1926441277	0.2065574703	-1.5238173146
P	-0.0716334957	0.0504225850	-0.9237323998
Si	-0.2740962049	-0.0844353621	1.3677073329

Frequencies

223.672
350.070
381.904
412.732
781.812
1041.909
1115.893
1136.296
2034.700
2446.816
2457.653
2514.620

E(D0) = -100.0
E(D1) = -101.3
E(D2) = -103.1
E(D3) = -102.9
E(D4) = -102.9

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01663792

i0: $HSi\text{--}PH_3$

H	-0.2207176500	-1.0879123200	-1.4049713600
H	-0.5270953800	0.8087543200	-0.6284608800
H	0.3257130400	1.4815076600	1.4744752600
H	0.9728553900	-0.3951979000	0.1361483900
P	0.5765628800	0.0516615300	-1.1712374700
Si	-0.6416853700	0.3142478800	1.4272713700

Frequencies

65.563
162.192
265.057
343.548
655.493
951.852
1111.291
1145.468
2063.710
2164.877
2233.850
2469.394

E(D0) = -18.8
E(D1) = -21.6
E(D2) = -21.0
E(D3) = -20.1
E(D4) = -21.0

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02006214

i2a: H_2SiPH_2

H	0.2322097806	1.4529579954	1.6383452670
H	-0.3663830305	-1.0669679681	-1.3928271458
H	0.9018850414	-0.8587118925	1.6516647502
H	-0.9422517275	0.9186247838	-1.4036824490
P	0.2383633547	0.1861629433	-1.1517416352
Si	-0.0570152987	0.1130627381	1.0779890428

Frequencies

158.843
452.987
479.077
524.340
735.192
787.855
922.332
1100.928
2229.478
2254.672
2444.957
2452.098

E(D0) = -188.8
E(D1) = -190.8
E(D2) = -191.4
E(D3) = -190.8
E(D4) = -191.4

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02023650

i2b: H_2SiPH_2

H	0.1338658964	-0.9466892928	1.8996698792
H	-0.3130016947	1.1458116300	-1.4667113207
H	-1.0377578416	-0.7772577458	-1.3428092833
H	-1.6633234274	0.5949848243	1.4175627660
P	0.1831179323	-0.1160371165	-1.0719851084
Si	-0.2617914450	0.2364493307	1.1085603972

Frequencies

137.610
450.852
483.843
501.866
716.100
760.843
934.107
1109.132
2239.574
2270.104
2427.695
2447.905

E(D0) = -182.8
E(D1) = -184.8
E(D2) = -185.5
E(D3) = -185.4
E(D4) = -184.8

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01739167

i3: H_3SiPH

H	-0.3013147031	-0.9474965529	-1.3684279205
H	0.5340240535	1.5449456987	1.5679876137
H	0.6604821264	-0.8565987306	1.6063138122

H	-1.4604096322	0.2297308095	1.2882594831
P	0.3243159918	0.3160765200	-1.2332608245
Si	-0.0150218964	0.3041401653	0.9899369259

Frequencies

182.667
457.617
479.791
497.603
774.992
912.234
954.071
959.613
2263.462
2269.295
2286.401
2421.308

E(D0) = -219.6
E(D1) = -221.6
E(D2) = -222.1
E(D3) = -222.0
E(D4) = -222.0

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01341163

TRANSITION STATES

i1 - i2b

H	0.0168331775	-1.1892504578	-0.3355083118
H	-1.0048334281	-0.4486423591	-1.9778890955
H	1.1249287940	-0.4339476203	-1.8954858551
H	-1.4596769080	-0.0231090736	1.1206178358
P	0.0267564651	0.0105794464	-1.1395745281
Si	0.0258881265	0.0848281160	1.4189226236

Frequencies

541.176 i
198.426
232.856
282.689
701.281
975.005
1065.753
1128.583
2049.513
2176.356
2476.796
2496.156

E(D0) = -22.1
E(D1) = -24.3
E(D2) = -24.6
E(D3) = -24.7
E(D4) = -24.3

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01940730

i0 - i2a

H	-0.1723824028	-1.1143657162	-1.3609868317
H	0.3971949191	1.4578915377	1.3474194612
H	0.5615592187	-0.6190937826	0.6646156579
H	-0.7378267824	0.6417214905	-0.4533966436
P	0.5271429607	0.0779968446	-1.0630759217
Si	-0.5688797935	0.3009782260	1.2851721080

Frequencies

515.550 i
288.231
427.394
583.110
755.240
880.743
918.911
1071.453
1693.013
1825.981
2111.154
2439.220

E(D0) = -7.1
E(D1) = -9.8
E(D2) = -9.1
E(D3) = -7.8
E(D4) = -9.2

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02892678

i0 - p3

H	0.7275997068	-1.2144188668	-1.1018111002
H	1.0112920026	0.8536085281	-1.0294771555
H	-1.0990574823	0.1089545229	0.2413591515
H	-1.4731732757	0.1426544327	1.3030615658
P	-0.0630600773	-0.0508083659	-1.1193356540
Si	0.0815103598	-0.2053271331	1.4251096524

Frequencies

998.805 i
43.488
348.668
553.210
648.894
732.376
984.163
1101.437
1590.970
1852.366
2467.970
2479.443

E(D0) = 27.6
E(D1) = 25.0
E(D2) = 25.0
E(D3) = 27.2
E(D4) = 26.3

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01681629

i1 - p2

H	-0.0138822567	-1.0327211646	-1.7898175468
H	-0.1956700193	0.9730578755	-2.2839367388
H	-0.3427142281	1.3128166536	1.2858147122
H	0.6127105699	0.8252693528	-1.7608683835
P	-0.5596622933	0.0475566723	-1.0696468315
Si	0.5139711989	0.0955576078	0.9993145187

Frequencies

1428.736 i
119.525
277.838
355.557
439.752
743.793
958.465
1101.711
1777.668
2062.327
2075.241
2469.805

E(D0) = 96.7
E(D1) = 93.8
E(D2) = 95.7
E(D3) = 95.3
E(D4) = 95.9

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02154789

i2a - i2b

H	0.1408185900	-0.9652959430	1.5949575143
H	0.3499864137	-0.8329306674	-1.3657210360
H	0.9227927644	1.3099511155	1.6790249708

H	-1.3604016051	0.3043140607	-1.3700060328
P	0.0215151553	0.5289542876	-1.1860803694
Si	-0.0679031983	0.4001357466	1.0675727831

Frequencies

150.038 i
451.438
510.287
553.368
698.323
729.668
940.135
1115.217
2243.905
2268.524
2443.374
2446.924

E(D0) = -182.2
E(D1) = -184.1
E(D2) = -184.8
E(D3) = -184.2
E(D4) = -184.8

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01837309

i2a - i3

H	-0.3342100316	-0.9816230126	-1.0890664759
H	0.5605347799	1.4360489798	1.8447635822
H	0.6663665545	-0.8558426732	0.7079834391
H	-1.6878522547	0.6356350603	1.1625836179
P	0.7640169723	-0.1274159810	-0.8269330937
Si	-0.2267800805	0.4839955368	1.0514780203

Frequencies

1445.637 i
346.344
498.309
501.255
551.246
748.335
905.434
1015.433

1642.487
2267.827
2320.969
2424.336

E(D0) = -90.9
E(D1) = -93.4
E(D2) = -93.1
E(D3) = -91.5
E(D4) = -92.9

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01522820

i2a - p3

H	0.1048208286	-0.9998535632	-1.2555396499
H	0.6545253087	-0.4461577903	1.2952361275
H	0.7833390160	0.5949529722	1.8539443776
H	-1.0705619963	0.6676831500	-1.6329417764
P	0.1517394517	0.3830555125	-0.9893675136
Si	-0.6170544887	0.5454483188	1.1484162649

Frequencies

1403.630 i
230.092
402.169
444.750
571.317
703.479
832.641
1129.195
1715.787
1853.683
2455.253
2460.367

E(D0) = -3.1
E(D1) = -5.7
E(D2) = -3.7
E(D3) = -3.9
E(D4) = -5.9

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02372143

i2b - p2

H	0.0603433409	1.8977366268	1.5085071270
H	0.4000579791	0.2264085464	-0.7553408027
H	0.6569368656	0.3597348461	3.0298580031
H	0.7835931699	1.3309179803	1.1009053281
P	1.0840780817	-0.4289792237	0.2983833112
Si	-0.3290584372	0.3729512241	1.9022180334

Frequencies

1499.640 i
382.487
430.318
508.712
675.278
859.690
887.717
976.210
1697.951
1852.900
2157.872
2415.519

E(D0) = -4.7
E(D1) = -6.3
E(D2) = -7.0
E(D3) = -6.9
E(D4) = -5.6

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02690564

i2b - p5

H	0.2238705892	-0.8133340815	2.1384972465
H	-0.4937855766	1.1000369091	-1.1589742827
H	-1.3518532140	0.9710977795	1.6249305791
H	-1.4581401494	-1.2741385052	-2.3243320337
P	0.4140785673	0.0612784878	-0.8349267179
Si	-0.2930607965	0.0923210402	1.0990925386

Frequencies

242.977 i
90.899
146.379

472.083
537.015
623.200
626.913
760.761
970.321
2286.650
2310.622
2422.215

E(D0) = 12.2
E(D1) = 10.0
E(D2) = 9.8
E(D3) = 10.1
E(D4) = 15.5

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01855560

i2b - p1

H	-0.6532098109	-1.0631809401	1.8712419984
H	1.2023231232	0.4974388882	1.6972188973
H	-1.5050586512	0.7673970916	-1.1788386229
H	-1.7525373534	-0.0059865894	-1.1876095433
P	0.0356433058	-0.2637190293	-1.1475042154
Si	0.2465365310	-0.3420985726	0.9538441958

Frequencies

961.101 i
284.033
361.766
435.137
528.768
582.025
642.245
965.857
1060.753
2273.017
2288.756
3314.957

E(D0) = 40.7
E(D1) = 38.7
E(D2) = 38.6
E(D3) = 39.6
E(D4) = 39.4

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.03236584

i3 - p4

H	-0.6325818133	-0.5779627247	-1.6018708969
H	0.6656507097	1.0319319747	1.7537786407
H	0.8076072997	-0.0463381507	1.5964728927
H	-1.3209168179	-0.2653322206	1.4553260651
P	0.6189110510	-0.1752825334	-1.0724914908
Si	-0.3965944891	0.6237815647	0.7195938791

Frequencies

1301.207 i
207.647
348.385
445.449
516.681
737.953
801.205
995.386
1719.391
2075.839
2254.492
2415.817

E(D0) = -1.6
E(D1) = -3.6
E(D2) = -3.0
E(D3) = -2.4
E(D4) = -3.7

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.02150631

i3 - p1

H	0.4330776560	1.2826406431	-0.2927386661
H	1.3942062807	1.2828398669	-0.5188724503
H	1.4224912636	-0.9660453482	-1.0949024631
H	1.9548001513	-0.2140787387	1.1652228708
P	-1.1362681435	0.1896115687	0.4405579331
Si	0.9408561220	-0.2373448717	0.0939853057

Frequencies

1578.973 i
323.348
523.130
661.817
712.549
902.525
933.089
1037.291
1699.858
1812.284
2263.087
2281.881

E(D0) = 88.3
E(D1) = 85.6
E(D2) = 85.1
E(D3) = 83.9
E(D4) = 83.9

CCSD(T)-F12/cc-pVQZ-F12 - T1 diagnostic: 0.01840769