Electronic Supplementary Information for Dalton Transactions

Unusual structural and energetic features of homolytic bond dissociation: from tetrakis(disyl)diphosphine to tetrakis(di-*tert*-butylsilyl)hydrazine

Konstantin B. Borisenko and David W. H. Rankin*

School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK; E-mail: D.W.H.Rankin@ed.ac.uk

Table S1 Optimised Cartesian coordinates for the lowest-energy conformer of the diphosphine $P_2[CH(SiMe_3)_2]_4$ from quantum chemical calculations.

B3LYP/3-21G*

P	1.170549	-0.087286	-0.139381
P	-1.170549	0.087286	-0.139381
C	-1.735388	-0.339194	1.651411
H	-1.012152	0.216508	2.275330
C	-1.793447	-1.405190	-1.171547
H	-2.312886	-2.033907	-0.434949
C	1.793447	1.405190	-1.171547
H	2.312886	2.033907	-0.434949
C	1.735388	0.339194	1.651411
H	1.012152	-0.216508	2.275330
Si	-3.390091	0.573442	2.081640
Si	-1.678884	-2.122340	2.381035
Si	-3.247820	-0.931325	-2.366226
Si	-0.623879	-2.674826	-2.021972
Si	0.623879	2.674826	-2.021972
Si	3.247820	0.931325	-2.366226

Si	3.390091	-0.573442	2.081640
Si	1.678884	2.122340	2.381035
C	0.094623	-2.750413	2.571625
H	0.078191	-3.822861	2.813855
H	0.691812	-2.621083	1.666678
H	0.605645	-2.236751	3.396466
C	-0.094623	2.750413	2.571625
H	-0.078191	3.822861	2.813855
H	-0.691812	2.621083	1.666678
H	-0.605645	2.236751	3.396466
C	-2.679294	-3.446074	1.453081
H	-3.666805	-3.093501	1.133721
H	-2.157127	-3.844751	0.577350
H	-2.840541	-4.285623	2.145591
C	2.679294	3.446074	1.453081
H	3.666805	3.093501	1.133721
H	2.157127	3.844751	0.577350
H	2.840541	4.285623	2.145591
C	-2.377896	-2.175269	4.148708
H	-3.465638	-2.044858	4.185345
H	-2.150426	-3.169393	4.560839
H	-1.921742	-1.429635	4.810942
C	2.377896	2.175269	4.148708
H	3.465638	2.044858	4.185345
H	2.150426	3.169393	4.560839
H	1.921742	1.429635	4.810942
C	-4.896398	-0.485919	1.634401
H	-4.929107	-1.417269	2.214031

H	-5.818926	0.071374	1.847898
H	-4.908618	-0.751964	0.571132
C	4.896398	0.485919	1.634401
H	4.929107	1.417269	2.214031
H	5.818926	-0.071374	1.847898
H	4.908618	0.751964	0.571132
C	-3.576235	2.274899	1.268754
H	-2.915837	3.003693	1.754455
H	-3.359185	2.285979	0.198929
H	-4.610639	2.620280	1.413734
C	3.576235	-2.274899	1.268754
H	2.915837	-3.003693	1.754455
H	3.359185	-2.285979	0.198929
H	4.610639	-2.620280	1.413734
C	-3.479762	0.967738	3.939551
H	-2.533810	1.386673	4.308805
H	-4.253210	1.734856	4.088946
H	-3.736742	0.108933	4.565165
C	3.479762	-0.967738	3.939551
H	2.533810	-1.386673	4.308805
H	4.253210	-1.734856	4.088946
H	3.736742	-0.108933	4.565165
C	-0.531378	3.632730	-0.871224
H	-1.038034	4.407913	-1.465418
H	-1.293066	2.979829	-0.438283
H	0.000000	4.138284	-0.056518
C	0.531378	-3.632730	-0.871224
H	1.038034	-4.407913	-1.465418

H	1.293066	-2.979829	-0.438283
H	0.000000	-4.138284	-0.056518
C	-0.448392	1.883326	-3.358041
H	0.136658	1.349264	-4.113553
H	-1.148381	1.174843	-2.904594
H	-1.040100	2.657394	-3.867304
C	0.448392	-1.883326	-3.358041
H	-0.136658	-1.349264	-4.113553
H	1.148381	-1.174843	-2.904594
H	1.040100	-2.657394	-3.867304
C	1.676118	4.052527	-2.811910
H	2.240928	4.601585	-2.045479
H	2.385529	3.707923	-3.569810
H	0.995963	4.771542	-3.291082
C	-1.676118	-4.052527	-2.811910
H	-2.240928	-4.601585	-2.045479
H	-2.385529	-3.707923	-3.569810
H	-0.995963	-4.771542	-3.291082
C	-4.025378	0.759276	-2.022900
H	-4.860784	0.904554	-2.723779
H	-4.426040	0.832732	-1.007679
H	-3.318078	1.583697	-2.166318
C	4.025378	-0.759276	-2.022900
H	4.860784	-0.904554	-2.723779
H	4.426040	-0.832732	-1.007679
H	3.318078	-1.583697	-2.166318
C	-2.835430	-0.906994	-4.220850
H	-3.770241	-0.708986	-4.765554

H	-2.133948	-0.104147	-4.474979
H	-2.425541	-1.848727	-4.598865
C	2.835430	0.906994	-4.220850
H	3.770241	0.708986	-4.765554
H	2.133948	0.104147	-4.474979
H	2.425541	1.848727	-4.598865
C	-4.627146	-2.212214	-2.108437
H	-5.017002	-2.177420	-1.082241
H	-5.465488	-1.995796	-2.785766
H	-4.294640	-3.237579	-2.304742
C	4.627146	2.212214	-2.108437
H	5.017002	2.177420	-1.082241
H	5.465488	1.995796	-2.785766
H	4.294640	3.237579	-2.304742

ONIOM/(MP2/6-31+G*:B3LYP/3-21G*)

P	0.490570	1.042710	-0.129179
P	-0.490570	-1.042710	-0.129179
C	-0.306855	-1.723292	1.641364
H	-0.581226	-0.862634	2.271423
C	0.644582	-2.163800	-1.164116
H	1.060445	-2.868727	-0.434066
C	-0.644582	2.163800	-1.164116
H	-1.060445	2.868727	-0.434066
C	0.306855	1.723292	1.641364
H	0.581226	0.862634	2.271423
Si	-1.743238	-2.950873	2.077317
Si	1.383139	-2.294752	2.372810

Si	-0.343392	-3.361292	-2.325858
Si	2.242999	-1.554222	-2.048835
Si	-2.242999	1.554222	-2.048835
Si	0.343392	3.361292	-2.325858
Si	1.743238	2.950873	2.077317
Si	-1.383139	2.294752	2.372810
C	2.617403	-0.870583	2.530824
H	3.608811	-1.279282	2.775009
H	2.714617	-0.283847	1.614867
H	2.335673	-0.190895	3.345595
C	-2.617403	0.870583	2.530824
H	-3.608811	1.279282	2.775009
H	-2.714617	0.283847	1.614867
H	-2.335673	0.190895	3.345595
C	2.255694	-3.716298	1.460664
H	1.573107	-4.517068	1.154204
H	2.810637	-3.382133	0.577892
H	2.986126	-4.157597	2.155133
C	-2.255694	3.716298	1.460664
H	-1.573107	4.517068	1.154204
H	-2.810637	3.382133	0.577892
H	-2.986126	4.157597	2.155133
C	1.186169	-2.932659	4.152645
H	0.702540	-3.914947	4.208008
H	2.194511	-3.038481	4.579072
H	0.626203	-2.240491	4.792845
C	-1.186169	2.932659	4.152645
H	-0.702540	3.914947	4.208008

H	-2.194511	3.038481	4.579072
H	-0.626203	2.240491	4.792845
C	-1.296707	-4.733471	1.619124
H	-0.447718	-5.102124	2.208696
H	-2.151902	-5.393783	1.818548
H	-1.038265	-4.834484	0.559684
C	1.296707	4.733471	1.619124
H	0.447718	5.102124	2.208696
H	2.151902	5.393783	1.818548
H	1.038265	4.834484	0.559684
C	-3.403931	-2.494314	1.286236
H	-3.902660	-1.718507	1.880513
H	-3.314392	-2.127178	0.262206
H	-4.058347	-3.378090	1.280434
C	3.403931	2.494314	1.286236
H	3.902660	1.718507	1.880513
H	3.314392	2.127178	0.262206
H	4.058347	3.378090	1.280434
C	-2.123995	-2.918550	3.940483
H	-2.180281	-1.890714	4.324181
H	-3.113547	-3.374101	4.090846
H	-1.406308	-3.470372	4.553136
C	2.123995	2.918550	3.940483
H	2.180281	1.890714	4.324181
H	3.113547	3.374101	4.090846
H	1.406308	3.470372	4.553136
C	-3.578139	0.815209	-0.932003
H	-4.482983	0.662650	-1.539227

H	-3.270557	-0.151238	-0.525823
H	-3.848760	1.473728	-0.098688
C	3.578139	-0.815209	-0.932003
H	4.482983	-0.662650	-1.539227
H	3.270557	0.151238	-0.525823
H	3.848760	-1.473728	-0.098688
C	-1.892865	0.291376	-3.407434
H	-1.187254	0.655635	-4.161000
H	-1.485440	-0.626984	-2.974198
H	-2.831487	0.030270	-3.917271
C	1.892865	-0.291376	-3.407434
H	1.187254	-0.655635	-4.161000
H	1.485440	0.626984	-2.974198
H	2.831487	-0.030270	-3.917271
C	-3.127614	3.054337	-2.821686
H	-3.427364	3.774792	-2.047561
H	-2.544427	3.593040	-3.574178
H	-4.047846	2.696185	-3.305672
C	3.127614	-3.054337	-2.821686
H	3.427364	-3.774792	-2.047561
H	2.544427	-3.593040	-3.574178
H	4.047846	-2.696185	-3.305672
C	-2.199636	-3.443787	-1.968863
H	-2.652569	-4.165685	-2.664516
H	-2.416335	-3.780713	-0.951249
H	-2.695704	-2.477730	-2.114625
C	2.199636	3.443787	-1.968863
H	2.652569	4.165685	-2.664516

H	2.416335	3.780713	-0.951249
H	2.695704	2.477730	-2.114625
C	-0.231063	-3.014706	-4.190928
H	-0.767253	-3.824279	-4.707822
H	-0.718340	-2.073193	-4.467345
H	0.791462	-2.996195	-4.580143
C	0.231063	3.014706	-4.190928
H	0.767253	3.824279	-4.707822
H	0.718340	2.073193	-4.467345
H	-0.791462	2.996195	-4.580143
C	0.343392	-5.113208	-2.059234
H	0.225376	-5.445742	-1.019777
H	-0.204960	-5.822551	-2.695484
H	1.406214	-5.189222	-2.314512
C	-0.343392	5.113208	-2.059234
H	-0.225376	5.445742	-1.019777
H	0.204960	5.822551	-2.695484
H	-1.406214	5.189222	-2.314512

Table S2 Optimised Cartesian coordinates for the A conformer of the phosphido radical $P[CH(SiMe_3)_2]_2$ from quantum chemical calculations in ground and excited states.

B3LYP/3-21G*

P	0.031513	0.056836	-1.431703
C	-1.739533	0.193436	-0.764740
H	-2.285569	0.391304	-1.712518
C	1.213502	0.007809	0.028494

H	0.665958	0.211474	0.961476
Si	-2.496120	-1.481499	-0.216519
Si	-2.171510	1.743052	0.277240
Si	2.088162	-1.686362	0.352073
Si	2.500773	1.429626	-0.174529
C	-1.899526	3.272056	-0.807480
H	-1.991352	4.195308	-0.218889
H	-0.919756	3.274798	-1.294068
H	-2.664944	3.304858	-1.595826
C	-1.224709	1.866834	1.913505
H	-1.345123	0.955005	2.513446
H	-0.153995	2.047361	1.782872
H	-1.633959	2.702293	2.499324
C	-4.005672	1.803128	0.764324
H	-4.255341	1.092708	1.561091
H	-4.228230	2.812547	1.140111
H	-4.673342	1.610507	-0.084324
C	-1.865557	-1.998528	1.492385
H	-2.237577	-1.307596	2.261349
H	-2.227607	-3.003872	1.748088
H	-0.773159	-2.009078	1.554619
C	-2.148147	-2.780422	-1.552112
H	-2.786715	-2.580650	-2.424670
H	-1.109612	-2.777879	-1.894088
H	-2.391203	-3.789383	-1.190775
C	-4.390306	-1.415793	-0.112785
H	-4.829868	-0.949143	-1.004670
H	-4.771542	-2.446084	-0.061028

H	-4.758956	-0.878774	0.766494
C	1.717485	3.153521	-0.231245
H	2.522174	3.901529	-0.179671
H	1.179081	3.313167	-1.172696
H	1.024525	3.353507	0.592994
C	3.449831	1.272260	-1.804323
H	4.139134	0.423314	-1.832830
H	2.748580	1.168551	-2.643490
H	4.034442	2.187837	-1.972222
C	3.687236	1.449825	1.308331
H	3.140717	1.670314	2.236070
H	4.222509	0.505191	1.452725
H	4.435846	2.242720	1.171255
C	1.193629	-3.195458	-0.355917
H	1.763411	-4.096159	-0.084732
H	0.173016	-3.320759	0.015213
H	1.150721	-3.147094	-1.451518
C	3.833744	-1.831110	-0.377997
H	4.257467	-2.795063	-0.061257
H	3.803362	-1.832400	-1.475205
H	4.522762	-1.043425	-0.057946
C	2.208387	-1.883097	2.234808
H	1.212621	-1.935541	2.695242
H	2.741185	-2.810129	2.488505
H	2.747190	-1.047982	2.699883

ONIOM/(MP2/6-31+G*:B3LYP/3-21G*)

P	0.030469	0.059245	-1.433898

C	-1.720843	0.194812	-0.762021
H	-2.276762	0.397735	-1.696755
C	1.201253	0.005010	0.019133
H	0.654816	0.208016	0.950636
Si	-2.489385	-1.475315	-0.219208
Si	-2.152371	1.743413	0.281412
Si	2.073197	-1.685695	0.354515
Si	2.492096	1.420966	-0.178842
C	-1.887271	3.271955	-0.805773
H	-1.972785	4.195320	-0.216405
H	-0.912133	3.273584	-1.301385
H	-2.659982	3.305609	-1.586986
C	-1.205209	1.870671	1.917451
H	-1.326765	0.959940	2.518946
H	-0.134306	2.050969	1.788509
H	-1.615337	2.707089	2.501339
C	-3.985408	1.802496	0.773125
H	-4.233430	1.091144	1.569580
H	-4.205928	2.811561	1.151145
H	-4.655709	1.612048	-0.073875
C	-1.873626	-1.997461	1.493455
H	-2.246935	-1.304190	2.259757
H	-2.243641	-3.000547	1.746607
H	-0.781873	-2.014704	1.563592
C	-2.143123	-2.774312	-1.555334
H	-2.781805	-2.572739	-2.427423
H	-1.104876	-2.773289	-1.897892
H	-2.387960	-3.783043	-1.194571

C	-4.384027	-1.400318	-0.127822
H	-4.815794	-0.928610	-1.020891
H	-4.769461	-2.429417	-0.083206
H	-4.756987	-0.865870	0.751108
C	1.717578	3.148774	-0.244308
H	2.526414	3.891871	-0.186395
H	1.189332	3.310086	-1.191226
H	1.018143	3.354592	0.572848
C	3.448778	1.258828	-1.803843
H	4.135596	0.407854	-1.828613
H	2.751414	1.157019	-2.646469
H	4.036972	2.172584	-1.969197
C	3.672127	1.442359	1.309377
H	3.122210	1.667058	2.234127
H	4.204973	0.497225	1.459151
H	4.422872	2.233359	1.172968
C	1.182008	-3.199526	-0.347903
H	1.752770	-4.097668	-0.070331
H	0.160593	-3.325074	0.020774
H	1.142434	-3.157027	-1.443861
C	3.821474	-1.838056	-0.368132
H	4.241374	-2.801390	-0.044429
H	3.795378	-1.845464	-1.465426
H	4.511495	-1.050578	-0.049845
C	2.188154	-1.873581	2.238636
H	1.191505	-1.924396	2.697251
H	2.720414	-2.799619	2.497110
H	2.726010	-1.036793	2.701699

CIS/3-21G*

P	-0.000615	-0.074891	-1.033051
C	1.858794	0.159591	-0.700324
H	2.216222	0.390512	-1.711719
C	-1.471051	-0.001795	0.179301
H	-0.999295	0.186224	1.148907
Si	2.227602	1.786061	0.242994
Si	2.744277	-1.456575	-0.205848
Si	-2.654809	1.461342	-0.170731
Si	-2.260605	-1.744672	0.299923
C	2.131458	-2.919930	-1.226207
H	2.711654	-3.809517	-0.984459
H	1.084144	-3.142138	-1.064292
H	2.262852	-2.723813	-2.289255
C	2.551725	-1.785915	1.643311
H	3.083906	-1.042389	2.233031
H	1.512986	-1.777308	1.958237
H	2.963504	-2.759749	1.901894
C	4.593585	-1.316172	-0.598849
H	5.123967	-0.635527	0.057673
H	5.058830	-2.295849	-0.499176
H	4.756169	-0.986761	-1.624083
C	1.178384	1.978355	1.801479
H	1.249160	1.101609	2.441981
H	1.541049	2.828964	2.376326
H	0.130867	2.155507	1.587193
C	1.979652	3.234194	-0.937778

H	2.792212	3.273768	-1.661620
H	1.048071	3.157155	-1.485952
H	1.976918	4.181143	-0.400683
C	4.031590	1.857751	0.811971
H	4.726504	1.758459	-0.017615
H	4.212354	2.828275	1.272667
H	4.276331	1.098691	1.549512
C	-1.152472	-2.903759	1.293477
H	-1.630178	-3.878164	1.384308
H	-0.185536	-3.053793	0.829345
H	-0.988334	-2.528254	2.302162
C	-2.582839	-2.492128	-1.400907
H	-3.259175	-1.887578	-1.998788
H	-1.661165	-2.617113	-1.961475
H	-3.038469	-3.474792	-1.286484
C	-3.909908	-1.696204	1.233279
H	-3.788547	-1.316321	2.245275
H	-4.669703	-1.097676	0.740062
H	-4.298142	-2.710705	1.313335
C	-1.802105	3.053746	-0.707907
H	-2.546404	3.847404	-0.766667
H	-1.032041	3.378817	-0.015791
H	-1.346126	2.949714	-1.686775
C	-3.866847	1.014853	-1.549208
H	-4.509982	1.866529	-1.763663
H	-3.336043	0.770096	-2.467382
H	-4.509175	0.174876	-1.302348
C	-3.596822	1.873002	1.419269

H	-2.907037	2.150986	2.215149
H	-4.252209	2.725829	1.248867
H	-4.210275	1.056530	1.783879

Table S3 Optimised Cartesian coordinates for the B conformer of the phosphido radical $P[CH(SiMe_3)_2]_2$ from quantum chemical calculations in ground and excited states.

B3LYP/3-21G*

P	0.000000	0.000000	0.982355
C	0.000000	1.464868	-0.192001
C	0.000000	-1.464868	-0.192001
H	-0.436652	1.140841	-1.153071
H	0.436652	-1.140841	-1.153071
Si	1.794847	1.996230	-0.605087
Si	-1.150901	2.856964	0.451561
Si	-1.794847	-1.996230	-0.605087
Si	1.150901	-2.856964	0.451561
C	0.273905	-3.999188	1.680883
H	-0.569104	-4.537663	1.230461
H	0.980285	-4.747176	2.066641
H	-0.108729	-3.430266	2.538934
C	2.660537	-2.133739	1.338788
H	2.370920	-1.627707	2.268206
H	3.370370	-2.933851	1.592451
H	3.188876	-1.401820	0.714594
C	1.774307	-3.857317	-1.032133
H	2.330170	-3.214468	-1.728946

H	2.455999	-4.652049	-0.698443
H	0.957169	-4.328896	-1.590444
C	2.609174	0.686312	-1.710077
H	2.043060	0.534456	-2.639495
H	3.622388	1.008745	-1.988517
H	2.696740	-0.282793	-1.204613
C	2.837485	2.188929	0.959763
H	2.852932	1.258920	1.541792
H	3.873593	2.441100	0.693959
H	2.455588	2.984240	1.610869
C	1.830367	3.630162	-1.569795
H	1.431640	4.467281	-0.983856
H	2.865777	3.877395	-1.843209
H	1.248050	3.560725	-2.498175
C	-0.273905	3.999188	1.680883
H	0.569104	4.537663	1.230461
H	-0.980285	4.747176	2.066641
H	0.108729	3.430266	2.538934
C	-2.660537	2.133739	1.338788
H	-2.370920	1.627707	2.268206
H	-3.370370	2.933851	1.592451
H	-3.188876	1.401820	0.714594
C	-1.774307	3.857317	-1.032133
H	-2.330170	3.214468	-1.728946
H	-2.455999	4.652049	-0.698443
H	-0.957169	4.328896	-1.590444
C	-2.609174	-0.686312	-1.710077
H	-2.043060	-0.534456	-2.639495

H	-3.622388	-1.008745	-1.988517
H	-2.696740	0.282793	-1.204613
C	-2.837485	-2.188929	0.959763
H	-2.852932	-1.258920	1.541792
H	-3.873593	-2.441100	0.693959
H	-2.455588	-2.984240	1.610869
C	-1.830367	-3.630162	-1.569795
H	-1.431640	-4.467281	-0.983856
H	-2.865777	-3.877395	-1.843209
H	-1.248050	-3.560725	-2.498175

ONIOM/(MP2/6-31+G*:B3LYP/3-21G*)

P	0.000000	0.000000	0.990514
C	0.000000	1.450113	-0.179139
C	0.000000	-1.450113	-0.179139
H	-0.441526	1.129312	-1.136032
H	0.441526	-1.129312	-1.136032
Si	1.791084	1.978922	-0.603020
Si	-1.146292	2.850410	0.451486
Si	-1.791084	-1.978922	-0.603020
Si	1.146292	-2.850410	0.451486
C	0.267265	-4.013317	1.660230
H	-0.575252	-4.544264	1.200239
H	0.973642	-4.767545	2.033698
H	-0.116015	-3.459254	2.527674
C	2.650778	-2.139648	1.357412
H	2.355804	-1.647889	2.292784
H	3.359151	-2.943651	1.602819

H	3.182734	-1.398336	0.747624
C	1.778511	-3.827816	-1.043851
H	2.334011	-3.173276	-1.730006
H	2.462490	-4.624071	-0.718583
H	0.965443	-4.295390	-1.611472
C	2.606343	0.662320	-1.699542
H	2.038352	0.500585	-2.626140
H	3.617232	0.987272	-1.983543
H	2.700146	-0.302127	-1.186587
C	2.837832	2.186072	0.957296
H	2.852503	1.262339	1.549271
H	3.873903	2.433259	0.686741
H	2.458905	2.989097	1.600640
C	1.823177	3.604054	-1.582808
H	1.425167	4.446477	-1.004141
H	2.857978	3.849109	-1.860478
H	1.239240	3.525651	-2.509480
C	-0.267265	4.013317	1.660230
H	0.575252	4.544264	1.200239
H	-0.973642	4.767545	2.033698
H	0.116015	3.459254	2.527674
C	-2.650778	2.139648	1.357412
H	-2.355804	1.647889	2.292784
H	-3.359151	2.943651	1.602819
H	-3.182734	1.398336	0.747624
C	-1.778511	3.827816	-1.043851
H	-2.334011	3.173276	-1.730006
H	-2.462490	4.624071	-0.718583

H	-0.965443	4.295390	-1.611472
C	-2.606343	-0.662320	-1.699542
H	-2.038352	-0.500585	-2.626140
H	-3.617232	-0.987272	-1.983543
H	-2.700146	0.302127	-1.186587
C	-2.837832	-2.186072	0.957296
H	-2.852503	-1.262339	1.549271
H	-3.873903	-2.433259	0.686741
H	-2.458905	-2.989097	1.600640
C	-1.823177	-3.604054	-1.582808
H	-1.425167	-4.446477	-1.004141
H	-2.857978	-3.849109	-1.860478
H	-1.239240	-3.525651	-2.509480

CIS/3-21G*

P	-0.000080	-0.000011	-0.567258
C	1.656422	-0.231228	0.292412
C	-1.656325	0.231245	0.292894
H	1.499468	-0.979795	1.072675
H	-1.499141	0.979838	1.073089
Si	2.265661	1.390161	1.077765
Si	2.789886	-1.144355	-0.960643
Si	-2.265356	-1.390114	1.078469
Si	-2.790149	1.144320	-0.959863
C	-2.651886	0.398386	-2.687019
H	-2.892202	-0.661125	-2.696363
H	-3.345083	0.899909	-3.360634
H	-1.653461	0.516559	-3.101310

C	-2.279148	2.958813	-1.020055
H	-1.230338	3.064945	-1.281695
H	-2.866324	3.497474	-1.761949
H	-2.437132	3.448018	-0.060457
C	-4.602579	1.074200	-0.429461
H	-4.751049	1.491415	0.563590
H	-5.200131	1.663929	-1.123098
H	-5.003860	0.064580	-0.432612
C	0.889452	2.255299	2.041819
H	0.414074	1.587035	2.757536
H	1.306047	3.089654	2.603990
H	0.122565	2.652697	1.384004
C	2.907248	2.576879	-0.239513
H	2.146218	2.760660	-0.993922
H	3.167953	3.534040	0.208404
H	3.794645	2.199846	-0.742272
C	3.634686	1.019009	2.333265
H	4.541011	0.636129	1.876077
H	3.898140	1.927945	2.872140
H	3.301389	0.290882	3.071271
C	2.651109	-0.398520	-2.687800
H	2.891430	0.660988	-2.697277
H	3.344102	-0.900087	-3.361592
H	1.652560	-0.516708	-3.101789
C	2.278867	-2.958851	-1.020587
H	1.229979	-3.064990	-1.281912
H	2.865820	-3.497558	-1.762623
H	2.437130	-3.448000	-0.061007

C	4.602476	-1.074212	-0.430791
H	4.751247	-1.491376	0.562236
H	5.199815	-1.663982	-1.124579
H	5.003763	-0.064597	-0.434121
C	-0.888877	-2.255271	2.042123
H	-0.413248	-1.587001	2.757667
H	-1.305332	-3.089588	2.604457
H	-0.122214	-2.652726	1.384083
C	-2.907378	-2.576843	-0.238586
H	-2.146599	-2.760639	-0.993243
H	-3.167935	-3.533996	0.209436
H	-3.794941	-2.199817	-0.741059
C	-3.633990	-1.018901	2.334376
H	-4.540434	-0.635978	1.877456
H	-3.897327	-1.927819	2.873336
H	-3.300435	-0.290783	3.072276

Table S4 Optimised Cartesian coordinates for the lowest-energy conformer of the hydrazine $N_2[SiH(CMe_3)_2]_4$ from quantum chemical calculations.

B3LYP/3-21G*

N	-0.005494	0.789930	-0.010063
Si	1.588432	1.601367	0.245982
Si	-1.431634	1.870638	-0.255537
C	1.901905	2.255978	2.058724
C	2.274470	2.887618	-1.064038
C	1.431634	3.724877	2.263143
C	3.402293	2.201449	2.484814

H	4.026706	2.899538	1.926932
H	3.468112	2.468870	3.549368
H	3.815848	1.197911	2.367117
C	1.147044	1.354167	3.069587
H	0.086428	1.290518	2.842494
H	1.556598	0.341201	3.065460
H	1.268706	1.761933	4.083203
C	1.537504	4.246153	-1.216237
H	1.422941	4.769866	-0.264262
H	2.119613	4.888692	-1.892532
H	0.546217	4.112150	-1.650873
C	2.372550	2.265808	-2.482818
H	2.849827	2.991524	-3.156756
H	2.976884	1.355459	-2.485771
H	1.388027	2.031176	-2.887476
C	3.745425	3.215483	-0.646596
H	4.333073	2.310556	-0.450992
H	4.225340	3.757511	-1.473121
H	3.781146	3.859013	0.235177
C	-2.813137	2.322425	1.068319
C	-2.189130	1.945840	-2.055183
C	-3.656728	1.450319	-2.172881
H	-3.776459	0.428663	-1.801290
H	-4.346720	2.099832	-1.628117
C	-1.329896	1.118212	-3.043096
H	-1.810359	1.114358	-4.031868
H	-0.337130	1.555220	-3.155606
H	-1.206901	0.091251	-2.708470

C	-2.161987	3.418337	-2.576590
H	-2.516058	3.429212	-3.617408
H	-2.806361	4.081503	-1.994391
H	-1.147667	3.826518	-2.562202
C	-3.302881	3.751396	0.656302
H	-3.886640	3.731676	-0.267365
H	-3.953875	4.137867	1.452682
H	-2.467175	4.449551	0.532986
H	2.049171	4.422230	1.689254
H	0.388605	3.869540	1.969976
H	1.527263	3.989162	3.325956
C	-2.227375	2.468748	2.496734
H	-1.373997	3.150159	2.522766
H	-3.003790	2.873086	3.161954
H	-1.914426	1.503510	2.897435
C	-4.076285	1.432196	1.192818
H	-4.594874	1.302274	0.242000
H	-3.827773	0.444950	1.579419
H	-3.952942	1.464475	-3.231422
H	-4.773734	1.904691	1.899942
H	-0.606795	3.106686	-0.121639
H	2.508293	0.442987	0.043631
N	0.005494	-0.789930	-0.010063
Si	-1.588432	-1.601367	0.245982
Si	1.431634	-1.870638	-0.255537
C	-1.901905	-2.255978	2.058724
C	-2.274470	-2.887618	-1.064038
C	-1.431634	-3.724877	2.263143

C	-3.402293	-2.201449	2.484814
H	-4.026706	-2.899538	1.926932
H	-3.468112	-2.468870	3.549368
H	-3.815848	-1.197911	2.367117
C	-1.147044	-1.354167	3.069587
H	-0.086428	-1.290518	2.842494
H	-1.556598	-0.341201	3.065460
H	-1.268706	-1.761933	4.083203
C	-1.537504	-4.246153	-1.216237
H	-1.422941	-4.769866	-0.264262
H	-2.119613	-4.888692	-1.892532
H	-0.546217	-4.112150	-1.650873
C	-2.372550	-2.265808	-2.482818
H	-2.849827	-2.991524	-3.156756
H	-2.976884	-1.355459	-2.485771
H	-1.388027	-2.031176	-2.887476
C	-3.745425	-3.215483	-0.646596
H	-4.333073	-2.310556	-0.450992
H	-4.225340	-3.757511	-1.473121
H	-3.781146	-3.859013	0.235177
C	2.813137	-2.322425	1.068319
C	2.189130	-1.945840	-2.055183
C	3.656728	-1.450319	-2.172881
H	3.776459	-0.428663	-1.801290
H	4.346720	-2.099832	-1.628117
C	1.329896	-1.118212	-3.043096
H	1.810359	-1.114358	-4.031868
H	0.337130	-1.555220	-3.155606

H	1.206901	-0.091251	-2.708470
C	2.161987	-3.418337	-2.576590
H	2.516058	-3.429212	-3.617408
H	2.806361	-4.081503	-1.994391
H	1.147667	-3.826518	-2.562202
C	3.302881	-3.751396	0.656302
H	3.886640	-3.731676	-0.267365
H	3.953875	-4.137867	1.452682
H	2.467175	-4.449551	0.532986
H	-2.049171	-4.422230	1.689254
H	-0.388605	-3.869540	1.969976
H	-1.527263	-3.989162	3.325956
C	2.227375	-2.468748	2.496734
H	1.373997	-3.150159	2.522766
H	3.003790	-2.873086	3.161954
H	1.914426	-1.503510	2.897435
C	4.076285	-1.432196	1.192818
H	4.594874	-1.302274	0.242000
H	3.827773	-0.444950	1.579419
H	3.952942	-1.464475	-3.231422
H	4.773734	-1.904691	1.899942
H	0.606795	-3.106686	-0.121639
H	-2.508293	-0.442987	0.043631

ONIOM/(MP2/6-31+G*:B3LYP/3-21G*)

N	-0.006948	0.758422	-0.013273
Si	1.593980	1.588196	0.250693
Si	-1.420932	1.879431	-0.261115

C	1.890251	2.245354	2.063107
C	2.262705	2.887541	-1.051754
C	1.420932	3.714911	2.263510
C	3.388941	2.191285	2.498314
H	4.017774	2.885160	1.939967
H	3.449442	2.464353	3.561735
H	3.801465	1.186319	2.388509
C	1.131494	1.346053	3.072205
H	0.072850	1.279465	2.838295
H	1.543494	0.334188	3.074094
H	1.245945	1.757614	4.085119
C	1.523008	4.244804	-1.201391
H	1.397285	4.762347	-0.247641
H	2.110612	4.892797	-1.867656
H	0.537097	4.111318	-1.647755
C	2.367736	2.273157	-2.473829
H	2.843902	3.004221	-3.142713
H	2.975764	1.365203	-2.479846
H	1.385382	2.036584	-2.882405
C	3.733044	3.221018	-0.631936
H	4.325340	2.318080	-0.440740
H	4.210622	3.769477	-1.455490
H	3.765274	3.860125	0.253218
C	-2.808459	2.321456	1.056116
C	-2.179926	1.940791	-2.058506
C	-3.647875	1.445309	-2.174183
H	-3.769060	0.426406	-1.795789
H	-4.338634	2.099318	-1.635951

C	-1.322900	1.106823	-3.042330
H	-1.806513	1.094345	-4.029496
H	-0.331168	1.544117	-3.161675
H	-1.197898	0.083073	-2.699342
C	-2.154532	3.409960	-2.591504
H	-2.510877	3.412967	-3.631587
H	-2.798022	4.077353	-2.012941
H	-1.140386	3.818987	-2.582880
C	-3.297501	3.751418	0.643090
H	-3.877300	3.732361	-0.283043
H	-3.951596	4.137538	1.437038
H	-2.461540	4.450245	0.523685
H	2.045089	4.411263	1.695844
H	0.381041	3.861780	1.961175
H	1.507589	3.978255	3.327306
C	-2.231560	2.469268	2.488480
H	-1.378169	3.150324	2.519989
H	-3.012320	2.874335	3.148164
H	-1.921882	1.504289	2.892199
C	-4.072329	1.431687	1.177718
H	-4.586884	1.296441	0.225755
H	-3.825767	0.446773	1.571422
H	-3.941815	1.452013	-3.233426
H	-4.772666	1.908227	1.879280
H	-0.584440	3.100538	-0.122168
H	2.512141	0.435462	0.045924
N	0.006948	-0.758422	-0.013273
Si	-1.593980	-1.588196	0.250693

Si	1.420932	-1.879431	-0.261115
C	-1.890251	-2.245354	2.063107
C	-2.262705	-2.887541	-1.051754
C	-1.420932	-3.714911	2.263510
C	-3.388941	-2.191285	2.498314
H	-4.017774	-2.885160	1.939967
H	-3.449442	-2.464353	3.561735
H	-3.801465	-1.186319	2.388509
C	-1.131494	-1.346053	3.072205
H	-0.072850	-1.279465	2.838295
H	-1.543494	-0.334188	3.074094
H	-1.245945	-1.757614	4.085119
C	-1.523008	-4.244804	-1.201391
H	-1.397285	-4.762347	-0.247641
H	-2.110612	-4.892797	-1.867656
H	-0.537097	-4.111318	-1.647755
C	-2.367736	-2.273157	-2.473829
H	-2.843902	-3.004221	-3.142713
H	-2.975764	-1.365203	-2.479846
H	-1.385382	-2.036584	-2.882405
C	-3.733044	-3.221018	-0.631936
H	-4.325340	-2.318080	-0.440740
H	-4.210622	-3.769477	-1.455490
H	-3.765274	-3.860125	0.253218
C	2.808459	-2.321456	1.056116
C	2.179926	-1.940791	-2.058506
C	3.647875	-1.445309	-2.174183
H	3.769060	-0.426406	-1.795789

H	4.338634	-2.099318	-1.635951
C	1.322900	-1.106823	-3.042330
H	1.806513	-1.094345	-4.029496
H	0.331168	-1.544117	-3.161675
H	1.197898	-0.083073	-2.699342
C	2.154532	-3.409960	-2.591504
H	2.510877	-3.412967	-3.631587
H	2.798022	-4.077353	-2.012941
H	1.140386	-3.818987	-2.582880
C	3.297501	-3.751418	0.643090
H	3.877300	-3.732361	-0.283043
H	3.951596	-4.137538	1.437038
H	2.461540	-4.450245	0.523685
H	-2.045089	-4.411263	1.695844
H	-0.381041	-3.861780	1.961175
H	-1.507589	-3.978255	3.327306
C	2.231560	-2.469268	2.488480
H	1.378169	-3.150324	2.519989
H	3.012320	-2.874335	3.148164
H	1.921882	-1.504289	2.892199
C	4.072329	-1.431687	1.177718
H	4.586884	-1.296441	0.225755
H	3.825767	-0.446773	1.571422
H	3.941815	-1.452013	-3.233426
H	4.772666	-1.908227	1.879280
H	0.584440	-3.100538	-0.122168
H	-2.512141	-0.435462	0.045924

Table S5 Optimised Cartesian coordinates for the lowest-energy conformer of the aminyl radical $N[SiH(CMe_3)_2]_2$ from quantum chemical calculations.

B3LYP/3-21G*

N	0.034567	0.173538	0.037213
Si	-1.627513	0.347481	0.433125
Si	1.659759	0.358533	-0.467685
C	-2.382010	-1.307835	1.038422
C	-2.529054	1.275408	-0.985200
C	-2.622483	-2.310527	-0.122560
C	-3.721997	-1.069494	1.791057
H	-4.495694	-0.667339	1.129845
H	-4.086277	-2.023320	2.197966
H	-3.586289	-0.374484	2.628834
C	-1.378852	-1.944486	2.042694
H	-0.413092	-2.136147	1.565912
H	-1.210444	-1.285500	2.903954
H	-1.785287	-2.895275	2.415102
C	-2.237242	0.618891	-2.364202
H	-2.650054	-0.394337	-2.424575
H	-2.695933	1.220309	-3.161774
H	-1.159044	0.566780	-2.553437
C	-1.964210	2.725860	-1.010694
H	-2.420733	3.282695	-1.841033
H	-2.189795	3.255556	-0.077314
H	-0.877988	2.723392	-1.154767
C	-4.064242	1.350735	-0.776415
H	-4.317499	1.806339	0.188817

H	-4.511625	1.966634	-1.569427
H	-4.523415	0.357394	-0.822126
C	2.362783	-1.332450	-1.030185
C	2.530502	1.279675	0.986591
C	2.274364	0.609026	2.361194
H	1.202763	0.551917	2.576496
H	2.686024	-0.405072	2.397238
C	1.967915	2.729823	1.026742
H	2.472797	3.294896	1.822909
H	2.140708	3.248741	0.076312
H	0.892155	2.730455	1.232590
C	4.059466	1.354338	0.727981
H	4.528286	1.968666	1.509840
H	4.519209	0.360717	0.757368
H	4.281738	1.813277	-0.243168
C	3.696357	-1.150148	-1.805699
H	4.492594	-0.765748	-1.159946
H	4.022807	-2.120935	-2.204873
H	3.572590	-0.460710	-2.649680
H	-3.359143	-1.926925	-0.837913
H	-1.691923	-2.520445	-0.663860
H	-3.002308	-3.260273	0.279636
C	1.325714	-1.966326	-2.005310
H	1.151381	-1.321191	-2.876034
H	1.703818	-2.932289	-2.368275
H	0.367553	-2.137229	-1.502226
C	2.581528	-2.306823	0.155786
H	3.353408	-1.937033	0.840420

H	1.655124	-2.447980	0.724050
H	2.757501	1.200876	3.151699
H	2.904759	-3.286865	-0.222797
H	1.818679	1.264308	-1.654044
H	-1.631981	1.253171	1.630405

ONIOM/(MP2/6-31+G*:B3LYP/3-21G*)

N	0.019464	-0.152308	0.154947
Si	-1.638249	0.372046	0.392908
Si	1.623966	0.299730	-0.369038
C	-2.599038	-1.107461	1.122408
C	-2.291937	1.160894	-1.227601
C	-2.781002	-2.234729	0.069870
C	-3.987397	-0.697852	1.687183
H	-4.662797	-0.351101	0.898757
H	-4.454679	-1.563922	2.176561
H	-3.890351	0.099678	2.434647
C	-1.748005	-1.668868	2.299208
H	-0.753645	-1.962605	1.949612
H	-1.629652	-0.920349	3.093669
H	-2.250532	-2.545825	2.730796
C	-1.921042	0.309851	-2.474181
H	-2.387618	-0.680682	-2.440284
H	-2.271090	0.820754	-3.382222
H	-0.836898	0.178763	-2.553298
C	-1.628498	2.561924	-1.375473
H	-1.975590	3.032789	-2.305914
H	-1.896937	3.217044	-0.538173

H	-0.536767	2.483527	-1.420286
C	-3.832713	1.356079	-1.196760
H	-4.147954	1.946329	-0.327559
H	-4.149191	1.891794	-2.102936
H	-4.357848	0.395215	-1.172828
C	2.463319	-1.275924	-1.040582
C	2.417698	1.198908	1.129047
C	2.176543	0.447938	2.466149
H	1.106509	0.330208	2.663712
H	2.633945	-0.546862	2.456436
C	1.779077	2.614465	1.230437
H	2.235646	3.160633	2.067732
H	1.946652	3.190780	0.312827
H	0.700155	2.552972	1.410183
C	3.946978	1.369638	0.911489
H	4.364178	1.964082	1.736689
H	4.459740	0.401819	0.899200
H	4.166189	1.893201	-0.027180
C	3.758294	-0.946646	-1.832204
H	4.530160	-0.514095	-1.187072
H	4.163222	-1.867917	-2.273935
H	3.554261	-0.241641	-2.647633
H	-3.418312	-1.908597	-0.760466
H	-1.812355	-2.549754	-0.337537
H	-3.254504	-3.108865	0.538180
C	1.459900	-1.957741	-2.017104
H	1.213162	-1.299869	-2.860351
H	1.907326	-2.875989	-2.422664

H	0.532355	-2.220990	-1.496834
C	2.787730	-2.277789	0.099024
H	3.546419	-1.876162	0.780642
H	1.886748	-2.510300	0.678762
H	2.622793	1.021156	3.291166
H	3.175928	-3.213257	-0.327545
H	1.591862	1.283735	-1.496620
H	-1.586251	1.439472	1.437499