**Supporting Information**

**Directed Gas Phase Preparation of Singlet Ethyl­silanediyl Carbene (HCCSiH; X1A') - The Isovalent Counterpart of Triplet Propargylene (HCCCH; X3B)**

Adam Rettig, Martin Head-Gordon\*

Department of Chemistry, University of   California, Berkeley, CA 94720, USA

Corresponding Author: [mhg@cchem.berkeley.edu](mailto:mhg@cchem.berkeley.edu)

Srinivas Doddipatla, Zhenghai Yang, Ralf I. Kaiser\*

*Department of Chemistry, University of Hawai’i at Manoa, Honolulu, Hawaii 96822, USA*

Corresponding Author: [ralfk@hawaii.edu](mailto:ralfk@hawaii.edu)

Table S: Geometries of intermediates computed via ωB97M-V//def2-tzvpd. Relative energies are computed via sMP3: ωB97M-V//CBS.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| A picture containing indoor, accessory  Description automatically generated | | | | A picture containing accessory  Description automatically generated | | | |
| [i1] | | | | [i2] | | | |
| C3v | | | | C2v | | | |
| -619.3 | | | | -576.8 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | -0.854274 | -1.501931 | -0.601048 | C | -1.385740 | 0.665319 | -0.947500 |
| C | -1.416438 | -2.489479 | -0.997117 | C | -1.385740 | -0.665320 | -0.947500 |
| H | 0.000000 | 0.000000 | 1.473943 | H | -2.015172 | 1.431230 | -1.377092 |
| H | 1.386926 | 0.000000 | -0.499099 | H | 0.000000 | 0.000000 | 1.473717 |
| H | -0.709797 | 1.191598 | -0.498997 | H | 1.373606 | 0.000000 | -0.534185 |
| H | -1.914724 | -3.362298 | -1.347914 | H | -2.015177 | -1.431231 | -1.377084 |
| A picture containing accessory  Description automatically generated | | | | A picture containing indoor, accessory, necklet  Description automatically generated | | | |
| [i3] | | | | [i4] | | | |
| Cs | | | | Cs | | | |
| -543.2 | | | | -537.7 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | 0.000000 | 0.000000 | 1.690359 | H | 0.000000 | 0.000000 | 1.521865 |
| C | -0.807437 | -0.001497 | 2.952639 | C | 1.873965 | 0.000000 | -0.104193 |
| H | 1.102362 | 0.000000 | 1.849234 | H | 2.357030 | 0.000604 | -1.080119 |
| H | -1.875503 | 0.002242 | 2.737876 | C | 2.675269 | -0.000729 | 0.966700 |
| H | -0.589058 | 0.874483 | 3.567211 | H | 2.264814 | -0.001335 | 1.970632 |
| H | -0.594195 | -0.882590 | 3.561763 | H | 3.759406 | -0.000733 | 0.885808 |
| A picture containing indoor, accessory, necklet  Description automatically generated | | | | A picture containing indoor, accessory  Description automatically generated | | | |
| [i5] | | | | [i6] | | | |
| C2v | | | | D2d | | | |
| -520.9 | | | | -462.8 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | -1.435609 | -0.005504 | -0.870819 | C | 0.000000 | 0.000000 | 1.681602 |
| C | -2.552493 | -0.009442 | -1.546599 | C | -0.019317 | 0.012310 | -1.681453 |
| H | 0.000000 | 0.000000 | 1.465207 | H | 0.923481 | 0.000000 | 2.242241 |
| H | 1.299293 | 0.000000 | -0.677274 | H | -0.924997 | -0.006593 | 2.239877 |
| H | -3.044370 | 0.912434 | -1.846159 | H | -0.016232 | -0.907247 | -2.248515 |
| H | -3.040616 | -0.934759 | -1.841662 | H | -0.023334 | 0.941160 | -2.233305 |
| A picture containing accessory, necklet  Description automatically generated | | | |
| [i7] | | | |
| Cs | | | |
| -437.9 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 |
| C | 0.000000 | 0.000000 | 1.617522 |
| C | -1.274405 | 0.000000 | -1.368558 |
| H | 0.493160 | 0.000000 | 2.572365 |
| H | -0.794681 | 0.008328 | -2.344394 |
| H | -1.902574 | 0.883529 | -1.268852 |
| H | -1.891939 | -0.892100 | -1.279003 |

Table S: Geometries of products computed via ωB97M-V//def2-tzvpd. Relative energies are computed via sMP3: ωB97M-V//CBS.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| A picture containing accessory  Description automatically generated | | | | A picture containing shape  Description automatically generated | | | |
| p1 | | | | p2 | | | |
| C2v | | | | C2v | | | |
| -486.9 | | | | -410.4 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | 0.000000 | 0.000000 | 1.817019 | C | 0.000000 | 0.000000 | 1.688304 |
| C | -1.244711 | 0.000000 | 1.323868 | C | 0.004466 | 0.000000 | 3.005001 |
| H | 0.422898 | 0.000000 | 2.812631 | H | 0.377646 | -0.843751 | 3.581926 |
| H | -2.234855 | 0.000000 | 1.759543 | H | -0.364252 | 0.843412 | 3.585310 |
| A picture containing indoor, lit, light, dark  Description automatically generated | | | |  | | | |
| p3 | | | | p4 | | | |
| Cs | | | | Cs | | | |
| -406.0 | | | | -321.7 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | 1.837023 | 0.000000 | -0.102990 | C | 1.860857 | 0.000000 | -0.560224 |
| C | 3.030036 | -0.000154 | -0.306592 | C | 1.976322 | 0.000054 | 0.691721 |
| H | 0.000000 | 0.000000 | 1.516063 | H | 0.000000 | 0.000000 | 1.537499 |
| H | 4.082213 | -0.000293 | -0.471476 | H | 2.312622 | 0.000139 | 1.706620 |
|  | | | | A picture containing accessory, necklet, dark  Description automatically generated | | | |
| p5 | | | | p6 | | | |
| C2v | | | | C2v | | | |
| -291.3 | | | | -263.8 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | -0.003946 | 0.000000 | -0.002651 |
| C | -1.389952 | 0.623924 | -0.995810 | C | -1.401693 | 0.000000 | -0.933726 |
| C | -1.389483 | -0.626390 | -0.995441 | C | -2.453402 | 0.000000 | -1.634145 |
| H | 0.000000 | 0.000000 | 1.471856 | H | -0.001566 | 0.000000 | 1.464801 |
| H | 1.393799 | 0.000000 | -0.472955 | H | 1.351148 | 0.000000 | -0.565841 |

Table :Geometries of transition states between intermediates computed via ωB97M-V//def2-tzvpd. Relative energies are computed via sMP3:ωB97M-V//CBS.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | | A picture containing dark  Description automatically generated | | | |
| [i1] → [i2] | | | | [i1] → [i5] | | | |
| Cs | | | | C1 | | | |
| -341.2 | | | | -347.7 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | -0.905563 | -1.492108 | -0.593622 | C | -1.457613 | -0.044499 | -1.073976 |
| C | -1.590068 | -2.392332 | -1.039303 | C | -1.335073 | -1.314056 | -0.618213 |
| H | 0.231986 | -1.635415 | 0.174963 | H | 0.000000 | 0.000000 | 1.472106 |
| H | 0.000000 | 0.000000 | 1.474913 | H | 1.378992 | 0.000000 | -0.522256 |
| H | 1.363533 | 0.000000 | -0.563492 | H | -1.722817 | -2.229280 | -1.059793 |
| H | -2.198545 | -3.167641 | -1.438338 | H | -0.727597 | -1.677895 | 0.324803 |
| A picture containing indoor, purple, lit, accessory  Description automatically generated | | | | A picture containing indoor, lit, purple, accessory  Description automatically generated | | | |
| [i2] → [i4] | | | | [i3] → [i4] | | | |
| C1 | | | | C1 | | | |
| -418.8 | | | | -429.2 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | 1.313987 | -1.723682 | -0.142780 | C | 1.727651 | -0.335722 | 0.120605 |
| C | 0.094397 | -1.932846 | -0.360950 | C | 1.711900 | 0.000000 | 1.491774 |
| H | 2.334544 | -2.006755 | 0.017354 | H | 1.555887 | -0.756931 | 2.250009 |
| H | 0.000000 | 0.000000 | 1.513813 | H | 2.175947 | 0.910193 | 1.877335 |
| H | 1.517476 | 0.000000 | -0.262374 | H | 0.000000 | 0.000000 | 1.592738 |
| H | -0.633836 | -2.699740 | -0.543994 | H | 2.504449 | -0.065333 | -0.578511 |
| A picture containing indoor, purple, lit, accessory  Description automatically generated | | | |
| [i4] → [i5] | | | |
| C1 | | | |
| -416.2 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 |
| C | 0.733589 | 1.613930 | -0.167785 |
| C | 1.300063 | 2.741027 | -0.475919 |
| H | 0.000000 | 0.000000 | 1.503368 |
| H | 1.527111 | 0.000000 | -0.300568 |
| H | 2.364349 | 2.901925 | -0.357420 |
| H | 0.692702 | 3.558949 | -0.848822 |

Table S: Geometries of transition states between intermediates and products computed via ωB97M-V//def2-tzvpd. Relative energies are computed via sMP3: ωB97M-V//CBS.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| A picture containing indoor  Description automatically generated | | | |  | | | |
| [i1] → p3 | | | | [i1] → p5 | | | |
| C1 | | | | Cs | | | |
| -368.9 | | | | -253.7 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | -0.888711 | 1.443961 | -0.674208 | C | -1.700902 | 0.398136 | -1.123744 |
| C | -1.572862 | 2.308346 | -1.159266 | C | -1.340547 | -0.783616 | -0.879820 |
| H | 1.352086 | 0.897109 | 0.216043 | H | -0.075837 | 1.748386 | -0.057228 |
| H | 0.000000 | 0.000000 | 1.474082 | H | -0.823191 | 1.567615 | -0.549988 |
| H | 1.433941 | 0.000000 | -0.485603 | H | 0.000000 | 0.000000 | 1.466637 |
| H | -2.167088 | 3.082572 | -1.583384 | H | 1.345671 | 0.000000 | -0.583354 |
| A close-up of a molecule  Description automatically generated with low confidence | | | | A picture containing accessory, lit, dark  Description automatically generated | | | |
| [i2] → p1 | | | | [i3] → p1 | | | |
| Cs | | | | C1 | | | |
| -270.6 | | | | -280.0 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | 0.873321 | -0.667969 | -1.436732 | C | 0.000000 | 0.000000 | 1.727005 |
| C | 0.873321 | 0.667972 | -1.436731 | C | -1.352955 | -0.313896 | 1.391217 |
| H | 0.000000 | 0.000000 | 1.484863 | H | 0.462079 | 0.000000 | 2.701028 |
| H | 1.277116 | -1.425052 | -2.093433 | H | -1.999840 | -1.126497 | 1.695625 |
| H | 1.231419 | 0.000000 | 1.209189 | H | -2.257603 | 0.632452 | 1.105559 |
| H | 1.277115 | 1.425055 | -2.093431 | H | -2.261452 | 0.664268 | 1.963708 |
| A picture containing indoor, lit, accessory, dark  Description automatically generated | | | | A picture containing indoor, lit, dark  Description automatically generated | | | |
| [i4] → p1 | | | | [i4] → p2 | | | |
| C1 | | | | C1 | | | |
| -336.5 | | | | -353.9 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | 1.846216 | 0.769674 | 0.305676 | C | 1.371373 | 1.066785 | 0.262273 |
| C | 0.955823 | 1.657330 | -0.043749 | C | 2.451987 | 1.807532 | 0.307760 |
| H | 0.000000 | 0.000000 | 1.665975 | H | 0.000000 | 0.000000 | 1.647367 |
| H | 2.922070 | 0.664101 | 0.289527 | H | 0.983695 | 0.000000 | 1.339072 |
| H | 0.971524 | 0.000000 | 1.359227 | H | 3.438883 | 1.383097 | 0.459499 |
| H | 0.998983 | 2.653771 | -0.456962 | H | 2.390549 | 2.886186 | 0.199770 |
| A picture containing accessory, necklet  Description automatically generated | | | |
| [i5] → p6 | | | |
| Cs | | | |
| -170.8 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 |
| C | -1.431315 | -0.094778 | -0.881376 |
| C | -2.510865 | 0.163091 | -1.538868 |
| H | 0.000000 | 0.000000 | 1.465210 |
| H | 1.308865 | 0.000000 | -0.658697 |
| H | -3.333039 | -0.693515 | -2.030707 |
| H | -2.886432 | -1.389510 | -1.763599 |

Table : Geometries of transition states between products computed via ωB97M-V//def2-tzvpd. Relative energies are computed via sMP3: ωB97M-V//CBS.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | | A picture containing indoor, dark  Description automatically generated | | | |
| p1 → p2 | | | | p1 → p3 | | | |
| C1 | | | | Cs | | | |
| -121.0 | | | | -121.9 | | | |
| Si | -0.062767 | -0.086183 | 0.073070 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | 0.026965 | 0.001523 | 1.814762 | C | 0.000000 | 0.000000 | 1.765972 |
| C | -0.047514 | 0.261554 | 3.134472 | C | -0.028708 | 0.001261 | 3.064140 |
| H | 1.121746 | 0.079120 | 2.282205 | H | 1.092270 | 0.000000 | 2.215600 |
| H | -0.241059 | -0.624165 | 3.756313 | H | 0.581793 | -0.020638 | 3.953872 |
| A picture containing indoor, dark  Description automatically generated | | | | A picture containing device, accessory  Description automatically generated | | | |
| p1 → p5 | | | | p3 → p4 | | | |
| Cs | | | | C1 | | | |
| -94.1 | | | | -318.3 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | -1.088881 | 0.079717 | -1.633286 | C | 1.871756 | 0.000000 | -0.406579 |
| C | -1.739954 | 0.104904 | -0.526823 | C | 2.162771 | -0.583517 | 0.642726 |
| H | 0.000000 | 0.000000 | 1.479743 | H | 0.000000 | 0.000000 | 1.536241 |
| H | 0.343083 | 0.000000 | -1.584918 | H | 2.504813 | -1.034226 | 1.549757 |
| A close-up of some light bulbs  Description automatically generated with low confidence | | | | A picture containing bubble chart  Description automatically generated | | | |
| p4 → p5 | | | | p5 → p6 | | | |
| Cs | | | | C1 | | | |
| -49.7 | | | | -263.9 | | | |
| Si | 0.000000 | 0.000000 | 0.000000 | Si | 0.000000 | 0.000000 | 0.000000 |
| C | 1.289444 | 0.000000 | -1.444773 | C | -1.397294 | 0.051727 | -0.933125 |
| C | -0.035347 | 0.000000 | -1.769526 | C | -2.318623 | -0.563657 | -1.541139 |
| H | 0.000000 | 0.000000 | 1.461972 | H | 0.000000 | 0.000000 | 1.468240 |
| H | 1.609119 | 0.000000 | -0.059355 | H | 1.356377 | 0.000000 | -0.562206 |

Table S: RRKM reaction rate constants and imaginary frequencies of transition states

|  |  |  |  |
| --- | --- | --- | --- |
| Reaction | kf (s-1) | kb (s-1) | ωb (cm-1) |
| [i1] → [i2] | 4.99E+10 | 1.20E+12 | -888 |
| [i1] → [i5] | 4.98E+09 | 4.84E+10 | -343 |
| [i2] → [i4] | 1.64E+12 | 1.34E+12 | -814 |
| [i3] → [i4] | 1.76E+11 | 3.22E+11 | -992 |
| [i4] → [i5] | 1.96E+12 | 9.63E+11 | -874 |
| [i1] → p3 | 1.10E+11 |  | -1218 |
| [i1] → p5 | 8.04E+08 |  | -1000 |
| [i2] → p1 | 1.72E+10 |  | -1610 |
| [i3] → p1 | 5.19E+09 |  | -1445 |
| [i4] → p1 | 6.70E+10 |  | -1469 |
| [i4] → p2 | 2.86E+11 |  | -1318 |
| [i5] → p6 | 1.80E+09 |  | -1070 |

Table S7: RRKM reaction rate constants and imaginary frequencies of transition states for product rearrangement assuming maximum possible internal energy of **p3**.

|  |  |  |  |
| --- | --- | --- | --- |
| Reaction | kf (s-1) | kb (s-1) | ωb (cm-1) |
| p1→ p2 | 1.09E+10 | 3.72E+10 | -718 |
| p1 → p3 | 2.11E+11 | 2.62E+10 | -1158 |
| p1 → p5 | 1.82E+10 | 4.21E+10 | -1581 |
| p3 → p4 | 9.88E+11 | 1.10E+13 | -335 |
| p4 → p5 | 9.77E+08 | 1.62E+09 | -1180 |
| p5 → p6 | 1.35E+13 | 1.82E+12 | -80 |



Figure S1: Complete potential energy surface of the reaction of C2 + SiH4 computed via sMP3: ωB97M-V//CBS. Relative energies are given in kJ mol-1.

Figure S2: Potential energy surface of SiC2H2 isomerization computed via sMP3: ωB97M-V//CBS. Relative energies are given in kJ mol-1.