

**The structural landscape in 14-vertex clusters of silicon,  $M@Si_{14}$ :  
when two bonding paradigms collide.**

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Supporting information

**Table S1.** Optimised coordinates and total energies for isomers A-C in Figure 2 (a) (PBE)

Ti @Si<sub>14</sub>

A: -71.12067520 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.074265  | -1.860682 | 1.671256  |
| 2.Si  | 2.556732  | -1.181686 | 0.000000  |
| 3.Si  | -0.254996 | -2.805038 | 0.000000  |
| 4.Si  | 1.074265  | -1.860682 | -1.671256 |
| 5.Si  | 2.556732  | 1.181686  | 0.000000  |
| 6.Si  | 1.074265  | 1.860682  | -1.671256 |
| 7.Si  | 0.000000  | 0.000000  | -2.711803 |
| 8.Si  | 0.000000  | 0.000000  | 2.711803  |
| 9.Si  | 1.074265  | 1.860682  | 1.671256  |
| 10.Si | -2.301736 | -1.623352 | 0.000000  |
| 11.Si | -2.148531 | 0.000000  | -1.671256 |
| 12.Si | -2.148531 | 0.000000  | 1.671256  |
| 13.Si | -2.301736 | 1.623352  | 0.000000  |
| 14.Si | -0.254996 | 2.805038  | 0.000000  |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

B: -70.91632315 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.624532 | -1.946832 |
| 2.Si  | 1.873600  | -2.045820 | -0.359734 |
| 3.Si  | 1.931906  | 0.000000  | -1.854162 |
| 4.Si  | 2.865439  | 0.000000  | 0.445235  |
| 5.Si  | 1.341401  | -1.244779 | 1.979526  |
| 6.Si  | 1.341401  | 1.244779  | 1.979526  |
| 7.Si  | 1.873600  | 2.045820  | -0.359734 |
| 8.Si  | -1.873600 | -2.045820 | -0.359734 |
| 9.Si  | -1.341401 | -1.244779 | 1.979526  |
| 10.Si | -1.931906 | 0.000000  | -1.854162 |
| 11.Si | 0.000000  | 1.624532  | -1.946832 |
| 12.Si | -2.865439 | 0.000000  | 0.445235  |
| 13.Si | -1.873600 | 2.045820  | -0.359734 |
| 14.Si | -1.341401 | 1.244779  | 1.979526  |
| 15.Ti | 0.000000  | 0.000000  | 0.129160  |

C: -70.78752108 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.372628  | 1.580212  | 1.584063  |
| 2.Si  | 1.373800  | -1.581983 | 1.580913  |
| 3.Si  | 1.373533  | -1.589188 | -1.587217 |
| 4.Si  | 1.379032  | 1.584051  | -1.581162 |
| 5.Si  | -1.372628 | -1.580212 | -1.584063 |
| 6.Si  | -1.379032 | -1.584051 | 1.581162  |
| 7.Si  | -1.373533 | 1.589188  | 1.587217  |
| 8.Si  | -1.373800 | 1.581983  | -1.580913 |
| 9.Si  | -0.002424 | -2.872062 | -0.001227 |
| 10.Si | 0.002424  | 2.872062  | 0.001227  |
| 11.Si | 2.545160  | -0.005818 | -0.013219 |
| 12.Si | -2.545160 | 0.005818  | 0.013219  |
| 13.Si | 0.001583  | -0.000866 | 2.869542  |
| 14.Si | -0.001583 | 0.000866  | -2.869542 |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

V@Si<sub>14</sub>

A: -73.07875358 eV doublet

|      |           |           |           |
|------|-----------|-----------|-----------|
| 1.Si | 1.114488  | -1.931255 | 1.837371  |
| 2.Si | 2.318058  | -1.187850 | 0.000000  |
| 3.Si | -0.132980 | -2.599031 | 0.000000  |
| 4.Si | 1.114488  | -1.931255 | -1.837371 |
| 5.Si | 2.546721  | 1.142047  | 0.000000  |

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 6.Si  | 1.061711  | 1.861975  | -1.637680 |
| 7.Si  | -0.011985 | 0.023328  | -2.643188 |
| 8.Si  | -0.011985 | 0.023328  | 2.643188  |
| 9.Si  | 1.061711  | 1.861975  | 1.637680  |
| 10.Si | -2.262199 | -1.628468 | 0.000000  |
| 11.Si | -2.152256 | 0.005599  | -1.653355 |
| 12.Si | -2.152256 | 0.005599  | 1.653355  |
| 13.Si | -2.258268 | 1.600817  | 0.000000  |
| 14.Si | -0.264279 | 2.789569  | 0.000000  |
| 15.V  | 0.016046  | -0.020678 | 0.000000  |

B: -73.16438907 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.040126  | -1.591277 | -1.948724 |
| 2.Si  | 1.814311  | -2.036404 | -0.309822 |
| 3.Si  | 1.907238  | 0.032563  | -1.832660 |
| 4.Si  | 2.819607  | 0.001201  | 0.456104  |
| 5.Si  | 1.215294  | -1.276514 | 1.947796  |
| 6.Si  | 1.269676  | 1.234851  | 1.946234  |
| 7.Si  | 1.824044  | 2.048177  | -0.337202 |
| 8.Si  | -1.824044 | -2.048177 | -0.337202 |
| 9.Si  | -1.269676 | -1.234851 | 1.946234  |
| 10.Si | -1.907238 | -0.032563 | -1.832660 |
| 11.Si | -0.040126 | 1.591277  | -1.948724 |
| 12.Si | -2.819607 | -0.001201 | 0.456104  |
| 13.Si | -1.814311 | 2.036404  | -0.309822 |
| 14.Si | -1.215294 | 1.276514  | 1.947796  |
| 15.V  | 0.000000  | 0.000000  | 0.085255  |

C: -72.62251998 eV quartet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.500310  | 1.500310  | 1.500310  |
| 2.Si  | 1.500310  | -1.500310 | 1.500310  |
| 3.Si  | 1.500310  | -1.500310 | -1.500310 |
| 4.Si  | 1.500310  | 1.500310  | -1.500310 |
| 5.Si  | -1.500310 | -1.500310 | -1.500310 |
| 6.Si  | -1.500310 | -1.500310 | 1.500310  |
| 7.Si  | -1.500310 | 1.500310  | 1.500310  |
| 8.Si  | -1.500310 | 1.500310  | -1.500310 |
| 9.Si  | 0.000000  | -2.735952 | 0.000000  |
| 10.Si | 0.000000  | 2.735952  | 0.000000  |
| 11.Si | 2.735952  | 0.000000  | 0.000000  |
| 12.Si | -2.735952 | 0.000000  | 0.000000  |
| 13.Si | 0.000000  | 0.000000  | 2.735952  |
| 14.Si | 0.000000  | 0.000000  | -2.735952 |
| 15.V  | 0.000000  | 0.000000  | 0.000000  |

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Cr@Si<sub>14</sub>

A: -74.57739689 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.126242  | -1.950709 | 1.798276  |
| 2.Si  | 2.334123  | -1.149388 | 0.000000  |
| 3.Si  | -0.171662 | -2.596103 | 0.000000  |
| 4.Si  | 1.126242  | -1.950709 | -1.798276 |
| 5.Si  | 2.334123  | 1.149388  | 0.000000  |
| 6.Si  | 1.126242  | 1.950709  | -1.798276 |
| 7.Si  | 0.000000  | 0.000000  | -2.527155 |
| 8.Si  | 0.000000  | 0.000000  | 2.527155  |
| 9.Si  | 1.126242  | 1.950709  | 1.798276  |
| 10.Si | -2.162460 | -1.446715 | 0.000000  |
| 11.Si | -2.252484 | 0.000000  | -1.798276 |
| 12.Si | -2.252484 | 0.000000  | 1.798276  |
| 13.Si | -2.162460 | 1.446715  | 0.000000  |
| 14.Si | -0.171662 | 2.596103  | 0.000000  |
| 15.Cr | 0.000000  | 0.000000  | 0.000000  |

B: -74.84701552 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.513017 | -1.988581 |
| 2.Si  | 1.735269  | -2.014983 | -0.313544 |
| 3.Si  | 1.996841  | 0.000000  | -1.821372 |
| 4.Si  | 2.776274  | 0.000000  | 0.488072  |
| 5.Si  | 1.224059  | -1.246337 | 1.947113  |
| 6.Si  | 1.224059  | 1.246337  | 1.947113  |
| 7.Si  | 1.735269  | 2.014983  | -0.313544 |
| 8.Si  | -1.735269 | -2.014983 | -0.313544 |
| 9.Si  | -1.224059 | -1.246337 | 1.947113  |
| 10.Si | -1.996841 | 0.000000  | -1.821372 |

|       |           |          |           |
|-------|-----------|----------|-----------|
| 11.Si | 0.000000  | 1.513017 | -1.988581 |
| 12.Si | -2.776274 | 0.000000 | 0.488072  |
| 13.Si | -1.735269 | 2.014983 | -0.313544 |
| 14.Si | -1.224059 | 1.246337 | 1.947113  |
| 15.Cr | 0.000000  | 0.000000 | 0.059346  |

C: -73.95329334 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.510439  | 1.490120  | 1.515675  |
| 2.Si  | 1.434446  | -1.416596 | 1.442357  |
| 3.Si  | 1.491032  | -1.480555 | -1.498479 |
| 4.Si  | 1.495936  | 1.492427  | -1.508626 |
| 5.Si  | -1.510439 | -1.490120 | -1.515675 |
| 6.Si  | -1.495936 | -1.492427 | 1.508626  |
| 7.Si  | -1.491032 | 1.480555  | 1.498479  |
| 8.Si  | -1.434446 | 1.416596  | -1.442357 |
| 9.Si  | -0.041504 | -2.703300 | -0.037407 |
| 10.Si | 0.041504  | 2.703300  | 0.037407  |
| 11.Si | 2.729033  | 0.040971  | -0.033513 |
| 12.Si | -2.729033 | -0.040971 | 0.033513  |
| 13.Si | -0.029483 | 0.033322  | 2.745950  |
| 14.Si | 0.029483  | -0.033322 | -2.745950 |
| 15.Cr | 0.000000  | 0.000000  | 0.000000  |

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Mn@Si<sub>14</sub>

A: -74.22270651 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.064155  | -1.842976 | 1.752268  |
| 2.Si  | 2.464074  | -1.226570 | 0.000000  |
| 3.Si  | -0.169228 | -2.745516 | 0.000000  |
| 4.Si  | 1.064155  | -1.842976 | -1.752268 |
| 5.Si  | 2.345502  | 1.099512  | 0.000000  |
| 6.Si  | 1.130480  | 1.944529  | -1.791247 |
| 7.Si  | -0.045059 | 0.077690  | -2.560278 |
| 8.Si  | -0.045059 | 0.077690  | 2.560278  |
| 9.Si  | 1.130480  | 1.944529  | 1.791247  |
| 10.Si | -2.120819 | -1.475131 | 0.000000  |
| 11.Si | -2.252502 | -0.009904 | -1.798022 |
| 12.Si | -2.252502 | -0.009904 | 1.798022  |
| 13.Si | -2.146474 | 1.432775  | 0.000000  |
| 14.Si | -0.175772 | 2.583242  | 0.000000  |
| 15.Mn | 0.004278  | -0.003760 | 0.000000  |

B: -74.49208668 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.437771 | -2.027568 |
| 2.Si  | 1.713047  | -2.030966 | -0.308795 |
| 3.Si  | 2.007834  | 0.000000  | -1.834971 |
| 4.Si  | 2.742221  | 0.000000  | 0.485013  |
| 5.Si  | 1.199989  | -1.232306 | 1.970320  |
| 6.Si  | 1.199989  | 1.232306  | 1.970320  |
| 7.Si  | 1.713047  | 2.030966  | -0.308795 |
| 8.Si  | -1.713047 | -2.030966 | -0.308795 |
| 9.Si  | -1.199989 | -1.232306 | 1.970320  |
| 10.Si | -2.007834 | 0.000000  | -1.834971 |
| 11.Si | 0.000000  | 1.437771  | -2.027568 |
| 12.Si | -2.742221 | 0.000000  | 0.485013  |
| 13.Si | -1.713047 | 2.030966  | -0.308795 |
| 14.Si | -1.199989 | 1.232306  | 1.970320  |
| 15.Mn | 0.000000  | 0.000000  | 0.059059  |

C: -74.25841328 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.454004  | 1.463539  | -1.460216 |
| 2.Si  | 1.472879  | -1.474326 | -1.464341 |
| 3.Si  | -1.465296 | -1.449916 | -1.459659 |
| 4.Si  | -1.522456 | 1.522234  | -1.516414 |
| 5.Si  | -1.454004 | -1.463539 | 1.460216  |
| 6.Si  | 1.522456  | -1.522234 | 1.516414  |
| 7.Si  | 1.465296  | 1.449916  | 1.459659  |
| 8.Si  | -1.472879 | 1.474326  | 1.464341  |
| 9.Si  | 0.036201  | -2.707460 | 0.024693  |
| 10.Si | -0.036201 | 2.707460  | -0.024693 |
| 11.Si | -0.024461 | 0.026033  | -2.699695 |
| 12.Si | 0.024461  | -0.026033 | 2.699695  |
| 13.Si | 2.707638  | -0.040353 | 0.023686  |
| 14.Si | -2.707638 | 0.040353  | -0.023686 |
| 15.Mn | 0.000000  | 0.000000  | 0.000000  |

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Fe@Si<sub>14</sub>

A: -73.34722100 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.089785  | -1.887563 | 1.772717  |
| 2.Si  | 2.413729  | -1.162718 | 0.000000  |
| 3.Si  | -0.199922 | -2.671710 | 0.000000  |
| 4.Si  | 1.089785  | -1.887563 | -1.772717 |
| 5.Si  | 2.413729  | 1.162718  | 0.000000  |
| 6.Si  | 1.089785  | 1.887563  | -1.772717 |
| 7.Si  | 0.000000  | 0.000000  | -2.605100 |
| 8.Si  | 0.000000  | 0.000000  | 2.605100  |
| 9.Si  | 1.089785  | 1.887563  | 1.772717  |
| 10.Si | -2.213808 | -1.508992 | 0.000000  |
| 11.Si | -2.179570 | 0.000000  | -1.772717 |
| 12.Si | -2.179570 | 0.000000  | 1.772717  |
| 13.Si | -2.213808 | 1.508992  | 0.000000  |
| 14.Si | -0.199922 | 2.671710  | 0.000000  |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

B: -73.71764648 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.395065 | -2.091550 |
| 2.Si  | 1.658420  | -2.029265 | -0.301767 |
| 3.Si  | 1.986502  | 0.000000  | -1.842716 |
| 4.Si  | 2.699864  | 0.000000  | 0.476905  |
| 5.Si  | 1.177955  | -1.212891 | 2.010764  |
| 6.Si  | 1.177955  | 1.212891  | 2.010764  |
| 7.Si  | 1.658420  | 2.029265  | -0.301767 |
| 8.Si  | -1.658420 | -2.029265 | -0.301767 |
| 9.Si  | -1.177955 | -1.212891 | 2.010764  |
| 10.Si | -1.986502 | 0.000000  | -1.842716 |
| 11.Si | 0.000000  | 1.395065  | -2.091550 |
| 12.Si | -2.699864 | 0.000000  | 0.476905  |
| 13.Si | -1.658420 | 2.029265  | -0.301767 |
| 14.Si | -1.177955 | 1.212891  | 2.010764  |
| 15.Fe | 0.000000  | 0.000000  | 0.043944  |

C: -74.31222706 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.492354  | 1.492354  | 1.492354  |
| 2.Si  | 1.492354  | -1.492354 | 1.492354  |
| 3.Si  | 1.492354  | -1.492354 | -1.492354 |
| 4.Si  | 1.492354  | 1.492354  | -1.492354 |
| 5.Si  | -1.492354 | -1.492354 | -1.492354 |
| 6.Si  | -1.492354 | -1.492354 | 1.492354  |
| 7.Si  | -1.492354 | 1.492354  | 1.492354  |
| 8.Si  | -1.492354 | 1.492354  | -1.492354 |
| 9.Si  | 0.000000  | -2.661251 | 0.000000  |
| 10.Si | 0.000000  | 2.661251  | 0.000000  |
| 11.Si | 2.661251  | 0.000000  | 0.000000  |
| 12.Si | -2.661251 | 0.000000  | 0.000000  |
| 13.Si | 0.000000  | 0.000000  | 2.661251  |
| 14.Si | 0.000000  | 0.000000  | -2.661251 |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

**Table S2.** Optimised coordinates and total energies for isomers A-C in Figure 2 (a) (BLYP)Ti@Si<sub>14</sub>

A: -61.00060802 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.093049  | -1.893217 | 1.688075  |
| 2.Si  | 2.596798  | -1.200274 | 0.000000  |
| 3.Si  | -0.258931 | -2.849030 | 0.000000  |
| 4.Si  | 1.093049  | -1.893217 | -1.688075 |
| 5.Si  | 2.596798  | 1.200274  | 0.000000  |
| 6.Si  | 1.093049  | 1.893217  | -1.688075 |
| 7.Si  | 0.000000  | 0.000000  | -2.739122 |
| 8.Si  | 0.000000  | 0.000000  | 2.739122  |
| 9.Si  | 1.093049  | 1.893217  | 1.688075  |
| 10.Si | -2.337867 | -1.648756 | 0.000000  |
| 11.Si | -2.186099 | 0.000000  | -1.688075 |
| 12.Si | -2.186099 | 0.000000  | 1.688075  |
| 13.Si | -2.337867 | 1.648756  | 0.000000  |
| 14.Si | -0.258931 | 2.849030  | 0.000000  |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

B: -60.18839738 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.666422 | -1.949707 |
| 2.Si  | 1.928144  | -2.075899 | -0.369676 |
| 3.Si  | 1.987035  | 0.000000  | -1.904238 |
| 4.Si  | 2.925333  | 0.000000  | 0.435491  |
| 5.Si  | 1.391025  | -1.259425 | 2.013368  |
| 6.Si  | 1.391025  | 1.259425  | 2.013368  |
| 7.Si  | 1.928144  | 2.075899  | -0.369676 |
| 8.Si  | -1.928144 | -2.075899 | -0.369676 |
| 9.Si  | -1.391025 | -1.259425 | 2.013368  |
| 10.Si | -1.987035 | 0.000000  | -1.904238 |
| 11.Si | 0.000000  | 1.666422  | -1.949707 |
| 12.Si | -2.925333 | 0.000000  | 0.435491  |
| 13.Si | -1.928144 | 2.075899  | -0.369676 |
| 14.Si | -1.391025 | 1.259425  | 2.013368  |
| 15.Ti | 0.000000  | 0.000000  | 0.146542  |

C: -60.04359999 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.400327  | 1.615050  | 1.617643  |
| 2.Si  | 1.399846  | -1.618298 | 1.615610  |
| 3.Si  | 1.398156  | -1.621797 | -1.621700 |
| 4.Si  | 1.403187  | 1.618285  | -1.617975 |
| 5.Si  | -1.400327 | -1.615050 | -1.617643 |
| 6.Si  | -1.403187 | -1.618285 | 1.617975  |
| 7.Si  | -1.398156 | 1.621797  | 1.621700  |
| 8.Si  | -1.399846 | 1.618298  | -1.615610 |
| 9.Si  | -0.002944 | -2.914798 | -0.000538 |
| 10.Si | 0.002944  | 2.914798  | 0.000538  |
| 11.Si | 2.577571  | -0.004811 | -0.009299 |
| 12.Si | -2.577571 | 0.004811  | 0.009299  |
| 13.Si | 0.000986  | -0.001848 | 2.914344  |
| 14.Si | -0.000986 | 0.001848  | -2.914344 |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

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V@Si<sub>14</sub>

A: -62.79590000 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.143450  | -1.985802 | 1.873342  |
| 2.Si  | 2.324249  | -1.201411 | 0.000000  |
| 3.Si  | -0.128438 | -2.614089 | 0.000000  |
| 4.Si  | 1.143450  | -1.985802 | -1.873342 |
| 5.Si  | 2.603094  | 1.162285  | 0.000000  |
| 6.Si  | 1.084868  | 1.899637  | -1.642309 |
| 7.Si  | -0.013130 | 0.031626  | -2.654870 |
| 8.Si  | -0.013130 | 0.031626  | 2.654870  |
| 9.Si  | 1.084868  | 1.899637  | 1.642309  |
| 10.Si | -2.290940 | -1.640799 | 0.000000  |
| 11.Si | -2.204916 | 0.001492  | -1.691209 |
| 12.Si | -2.204916 | 0.001492  | 1.691209  |
| 13.Si | -2.272010 | 1.595719  | 0.000000  |
| 14.Si | -0.274305 | 2.843186  | 0.000000  |
| 15.V  | 0.009881  | -0.022007 | 0.000000  |

B: -62.21166844 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.122692  | -1.625095 | -1.963747 |
| 2.Si  | 1.862910  | -2.083625 | -0.280646 |
| 3.Si  | 1.959172  | 0.094483  | -1.880915 |
| 4.Si  | 2.869247  | -0.010406 | 0.434469  |
| 5.Si  | 1.193465  | -1.325484 | 1.969536  |
| 6.Si  | 1.315314  | 1.206888  | 1.985221  |
| 7.Si  | 1.886926  | 2.089087  | -0.331838 |
| 8.Si  | -1.886926 | -2.089087 | -0.331838 |
| 9.Si  | -1.315314 | -1.206888 | 1.985221  |
| 10.Si | -1.959172 | -0.094483 | -1.880915 |
| 11.Si | -0.122692 | 1.625095  | -1.963747 |
| 12.Si | -2.869247 | 0.010406  | 0.434469  |
| 13.Si | -1.862910 | 2.083625  | -0.280646 |
| 14.Si | -1.193465 | 1.325484  | 1.969536  |
| 15.V  | 0.000000  | 0.000000  | 0.073883  |

C: -61.63855432 eV quartet

|      |          |           |          |
|------|----------|-----------|----------|
| 1.Si | 1.540902 | 1.540902  | 1.540902 |
| 2.Si | 1.540902 | -1.540902 | 1.540902 |

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 3.Si  | 1.540902  | -1.540902 | -1.540902 |
| 4.Si  | 1.540902  | 1.540902  | -1.540902 |
| 5.Si  | -1.540902 | -1.540902 | -1.540902 |
| 6.Si  | -1.540902 | -1.540902 | 1.540902  |
| 7.Si  | -1.540902 | 1.540902  | 1.540902  |
| 8.Si  | -1.540902 | 1.540902  | -1.540902 |
| 9.Si  | 0.000000  | -2.753345 | 0.000000  |
| 10.Si | 0.000000  | 2.753345  | 0.000000  |
| 11.Si | 2.753345  | 0.000000  | 0.000000  |
| 12.Si | -2.753345 | 0.000000  | 0.000000  |
| 13.Si | 0.000000  | 0.000000  | 2.753345  |
| 14.Si | 0.000000  | 0.000000  | -2.753345 |
| 15.V  | 0.000000  | 0.000000  | 0.000000  |

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Cr@Si<sub>14</sub>

A: -64.23458415 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.149571  | -1.991116 | 1.819448  |
| 2.Si  | 2.364299  | -1.163743 | 0.000000  |
| 3.Si  | -0.174318 | -2.629415 | 0.000000  |
| 4.Si  | 1.149571  | -1.991116 | -1.819448 |
| 5.Si  | 2.364299  | 1.163743  | 0.000000  |
| 6.Si  | 1.149571  | 1.991116  | -1.819448 |
| 7.Si  | 0.000000  | 0.000000  | -2.544447 |
| 8.Si  | 0.000000  | 0.000000  | 2.544447  |
| 9.Si  | 1.149571  | 1.991116  | 1.819448  |
| 10.Si | -2.189981 | -1.465672 | 0.000000  |
| 11.Si | -2.299143 | 0.000000  | -1.819448 |
| 12.Si | -2.299143 | 0.000000  | 1.819448  |
| 13.Si | -2.189981 | 1.465672  | 0.000000  |
| 14.Si | -0.174318 | 2.629415  | 0.000000  |
| 15.Cr | 0.000000  | 0.000000  | 0.000000  |

B: -63.75238289 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.566473 | -1.993655 |
| 2.Si  | 1.793407  | -2.046813 | -0.315795 |
| 3.Si  | 2.036474  | 0.000000  | -1.858039 |
| 4.Si  | 2.830756  | 0.000000  | 0.485569  |
| 5.Si  | 1.244540  | -1.266013 | 1.971019  |
| 6.Si  | 1.244540  | 1.266013  | 1.971019  |
| 7.Si  | 1.793407  | 2.046813  | -0.315795 |
| 8.Si  | -1.793407 | -2.046813 | -0.315795 |
| 9.Si  | -1.244540 | -1.266013 | 1.971019  |
| 10.Si | -2.036474 | 0.000000  | -1.858039 |
| 11.Si | 0.000000  | 1.566473  | -1.993655 |
| 12.Si | -2.830756 | 0.000000  | 0.485569  |
| 13.Si | -1.793407 | 2.046813  | -0.315795 |
| 14.Si | -1.244540 | 1.266013  | 1.971019  |
| 15.Cr | 0.000000  | 0.000000  | 0.060352  |

C: -62.90703769 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.550814  | 1.546333  | 1.549986  |
| 2.Si  | 1.461580  | -1.450038 | 1.468854  |
| 3.Si  | 1.533051  | -1.527770 | -1.551208 |
| 4.Si  | 1.548163  | 1.539528  | -1.544713 |
| 5.Si  | -1.550814 | -1.546333 | -1.549986 |
| 6.Si  | -1.548163 | -1.539528 | 1.544713  |
| 7.Si  | -1.533051 | 1.527770  | 1.551208  |
| 8.Si  | -1.461580 | 1.450038  | -1.468854 |
| 9.Si  | -0.040339 | -2.725416 | -0.038518 |
| 10.Si | 0.040339  | 2.725416  | 0.038518  |
| 11.Si | 2.740458  | 0.039744  | -0.035651 |
| 12.Si | -2.740458 | -0.039744 | 0.035651  |
| 13.Si | -0.031951 | 0.034505  | 2.753621  |
| 14.Si | 0.031951  | -0.034505 | -2.753621 |
| 15.Cr | 0.000000  | 0.000000  | 0.000000  |

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Mn@Si<sub>14</sub>

A: -63.93820283 eV doublet

|      |           |           |           |
|------|-----------|-----------|-----------|
| 1.Si | 1.088207  | -1.883548 | 1.770063  |
| 2.Si | 2.503081  | -1.237469 | 0.000000  |
| 3.Si | -0.178055 | -2.785502 | 0.000000  |
| 4.Si | 1.088207  | -1.883548 | -1.770063 |
| 5.Si | 2.376751  | 1.117565  | 0.000000  |

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 6.Si  | 1.143684  | 1.976982  | -1.807293 |
| 7.Si  | -0.037782 | 0.071808  | -2.581913 |
| 8.Si  | -0.037782 | 0.071808  | 2.581913  |
| 9.Si  | 1.143684  | 1.976982  | 1.807293  |
| 10.Si | -2.166132 | -1.510856 | 0.000000  |
| 11.Si | -2.276541 | -0.004274 | -1.801440 |
| 12.Si | -2.276541 | -0.004274 | 1.801440  |
| 13.Si | -2.186392 | 1.477405  | 0.000000  |
| 14.Si | -0.185518 | 2.619636  | 0.000000  |
| 15.Mn | 0.000489  | -0.001584 | 0.000000  |

B: -63.38949970 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.494332 | -2.017472 |
| 2.Si  | 1.778410  | -2.071068 | -0.304587 |
| 3.Si  | 2.039541  | 0.000000  | -1.895390 |
| 4.Si  | 2.790253  | 0.000000  | 0.457078  |
| 5.Si  | 1.220552  | -1.248377 | 2.000432  |
| 6.Si  | 1.220552  | 1.248377  | 2.000432  |
| 7.Si  | 1.778410  | 2.071068  | -0.304587 |
| 8.Si  | -1.778410 | -2.071068 | -0.304587 |
| 9.Si  | -1.220552 | -1.248377 | 2.000432  |
| 10.Si | -2.039541 | 0.000000  | -1.895390 |
| 11.Si | 0.000000  | 1.494332  | -2.017472 |
| 12.Si | -2.790253 | 0.000000  | 0.457078  |
| 13.Si | -1.778410 | 2.071068  | -0.304587 |
| 14.Si | -1.220552 | 1.248377  | 2.000432  |
| 15.Mn | 0.000000  | 0.000000  | 0.068855  |

C: -63.15404729 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.470790  | 1.504385  | -1.503158 |
| 2.Si  | 1.508351  | -1.510318 | -1.475764 |
| 3.Si  | -1.506047 | -1.468757 | -1.502914 |
| 4.Si  | -1.576175 | 1.578338  | -1.571358 |
| 5.Si  | -1.470790 | -1.504385 | 1.503158  |
| 6.Si  | 1.576175  | -1.578338 | 1.571358  |
| 7.Si  | 1.506047  | 1.468757  | 1.502914  |
| 8.Si  | -1.508351 | 1.510318  | 1.475764  |
| 9.Si  | 0.037629  | -2.729985 | 0.033519  |
| 10.Si | -0.037629 | 2.729985  | -0.033519 |
| 11.Si | -0.035175 | 0.035935  | -2.724640 |
| 12.Si | 0.035175  | -0.035935 | 2.724640  |
| 13.Si | 2.729205  | -0.041468 | 0.033051  |
| 14.Si | -2.729205 | 0.041468  | -0.033051 |
| 15.Mn | 0.000000  | 0.000000  | 0.000000  |

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Fe@Si<sub>14</sub>

A: -63.25262678 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.107105  | -1.917562 | 1.782737  |
| 2.Si  | 2.466020  | -1.178388 | 0.000000  |
| 3.Si  | -0.212496 | -2.724831 | 0.000000  |
| 4.Si  | 1.107105  | -1.917562 | -1.782737 |
| 5.Si  | 2.466020  | 1.178388  | 0.000000  |
| 6.Si  | 1.107105  | 1.917562  | -1.782737 |
| 7.Si  | 0.000000  | 0.000000  | -2.628708 |
| 8.Si  | 0.000000  | 0.000000  | 2.628708  |
| 9.Si  | 1.107105  | 1.917562  | 1.782737  |
| 10.Si | -2.253524 | -1.546442 | 0.000000  |
| 11.Si | -2.214210 | 0.000000  | -1.782737 |
| 12.Si | -2.214210 | 0.000000  | 1.782737  |
| 13.Si | -2.253524 | 1.546442  | 0.000000  |
| 14.Si | -0.212496 | 2.724831  | 0.000000  |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

B: -62.65923406 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.477690 | -2.066592 |
| 2.Si  | 1.729516  | -2.076623 | -0.277634 |
| 3.Si  | 1.989583  | 0.000000  | -1.927217 |
| 4.Si  | 2.748236  | 0.000000  | 0.417181  |
| 5.Si  | 1.196113  | -1.226329 | 2.041925  |
| 6.Si  | 1.196113  | 1.226329  | 2.041925  |
| 7.Si  | 1.729516  | 2.076623  | -0.277634 |
| 8.Si  | -1.729516 | -2.076623 | -0.277634 |
| 9.Si  | -1.196113 | -1.226329 | 2.041925  |
| 10.Si | -1.989583 | 0.000000  | -1.927217 |

|       |           |          |           |
|-------|-----------|----------|-----------|
| 11.Si | 0.000000  | 1.477690 | -2.066592 |
| 12.Si | -2.748236 | 0.000000 | 0.417181  |
| 13.Si | -1.729516 | 2.076623 | -0.277634 |
| 14.Si | -1.196113 | 1.226329 | 2.041925  |
| 15.Fe | 0.000000  | 0.000000 | 0.052625  |

C: -63.27030072 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.525719  | 1.525719  | 1.525719  |
| 2.Si  | 1.525719  | -1.525719 | 1.525719  |
| 3.Si  | 1.525719  | -1.525719 | -1.525719 |
| 4.Si  | 1.525719  | 1.525719  | -1.525719 |
| 5.Si  | -1.525719 | -1.525719 | -1.525719 |
| 6.Si  | -1.525719 | -1.525719 | 1.525719  |
| 7.Si  | -1.525719 | 1.525719  | 1.525719  |
| 8.Si  | -1.525719 | 1.525719  | -1.525719 |
| 9.Si  | 0.000000  | -2.682038 | 0.000000  |
| 10.Si | 0.000000  | 2.682038  | 0.000000  |
| 11.Si | 2.682038  | 0.000000  | 0.000000  |
| 12.Si | -2.682038 | 0.000000  | 0.000000  |
| 13.Si | 0.000000  | 0.000000  | 2.682038  |
| 14.Si | 0.000000  | 0.000000  | -2.682038 |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

**Table S3.** Optimised coordinates and total energies for isomers A-C in Figure 2 (c) (B3LYP)

Ti@Si<sub>14</sub>:

A: -76.61984643 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.082035  | -1.874139 | 1.666745  |
| 2.Si  | 2.568193  | -1.181118 | 0.000000  |
| 3.Si  | -0.261218 | -2.814680 | 0.000000  |
| 4.Si  | 1.082035  | -1.874139 | -1.666745 |
| 5.Si  | 2.568193  | 1.181118  | 0.000000  |
| 6.Si  | 1.082035  | 1.874139  | -1.666745 |
| 7.Si  | 0.000000  | 0.000000  | -2.716112 |
| 8.Si  | 0.000000  | 0.000000  | 2.716112  |
| 9.Si  | 1.082035  | 1.874139  | 1.666745  |
| 10.Si | -2.306975 | -1.633561 | 0.000000  |
| 11.Si | -2.164069 | 0.000000  | -1.666745 |
| 12.Si | -2.164069 | 0.000000  | 1.666745  |
| 13.Si | -2.306975 | 1.633561  | 0.000000  |
| 14.Si | -0.261218 | 2.814680  | 0.000000  |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

B: -75.63303100 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.644674 | -1.974293 |
| 2.Si  | 1.903765  | -2.059800 | -0.358770 |
| 3.Si  | 1.959163  | 0.000000  | -1.874765 |
| 4.Si  | 2.891849  | 0.000000  | 0.438530  |
| 5.Si  | 1.358442  | -1.248916 | 2.004583  |
| 6.Si  | 1.358442  | 1.248916  | 2.004583  |
| 7.Si  | 1.903765  | 2.059800  | -0.358770 |
| 8.Si  | -1.903765 | -2.059800 | -0.358770 |
| 9.Si  | -1.358442 | -1.248916 | 2.004583  |
| 10.Si | -1.959163 | 0.000000  | -1.874765 |
| 11.Si | 0.000000  | 1.644674  | -1.974293 |
| 12.Si | -2.891849 | 0.000000  | 0.438530  |
| 13.Si | -1.903765 | 2.059800  | -0.358770 |
| 14.Si | -1.358442 | 1.248916  | 2.004583  |
| 15.Ti | 0.000000  | 0.000000  | 0.132340  |

C: -75.49103638 eV singlet

|      |           |           |           |
|------|-----------|-----------|-----------|
| 1.Si | 1.386793  | 1.597072  | 1.600173  |
| 2.Si | 1.386530  | -1.600156 | 1.598204  |
| 3.Si | 1.385179  | -1.604780 | -1.604572 |
| 4.Si | 1.390127  | 1.600963  | -1.600306 |
| 5.Si | -1.386793 | -1.597072 | -1.600173 |
| 6.Si | -1.390127 | -1.600963 | 1.600306  |
| 7.Si | -1.385179 | 1.604780  | 1.604572  |
| 8.Si | -1.386530 | 1.600156  | -1.598204 |
| 9.Si | -0.002682 | -2.890639 | -0.000645 |



|       |           |           |           |
|-------|-----------|-----------|-----------|
| 10.Si | 0.002682  | 2.890639  | 0.000645  |
| 11.Si | 2.555927  | -0.005084 | -0.010338 |
| 12.Si | -2.555927 | 0.005084  | 0.010338  |
| 13.Si | 0.000394  | -0.001683 | 2.890420  |
| 14.Si | -0.000394 | 0.001683  | -2.890420 |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

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V@Si<sub>14</sub>

A: -79.10555381 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.148062  | -1.989655 | 1.876427  |
| 2.Si  | 2.273135  | -1.188233 | 0.000000  |
| 3.Si  | -0.109355 | -2.562898 | 0.000000  |
| 4.Si  | 1.148062  | -1.989655 | -1.876427 |
| 5.Si  | 2.590265  | 1.143941  | 0.000000  |
| 6.Si  | 1.065474  | 1.870927  | -1.617361 |
| 7.Si  | -0.017068 | 0.031972  | -2.643292 |
| 8.Si  | -0.017068 | 0.031972  | 2.643292  |
| 9.Si  | 1.065474  | 1.870927  | 1.617361  |
| 10.Si | -2.280647 | -1.663587 | 0.000000  |
| 11.Si | -2.158414 | 0.009870  | -1.629799 |
| 12.Si | -2.158414 | 0.009870  | 1.629799  |
| 13.Si | -2.279329 | 1.630616  | 0.000000  |
| 14.Si | -0.280590 | 2.808341  | 0.000000  |
| 15.V  | 0.005822  | -0.008612 | 0.000000  |

B: -78.38770394 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.082305  | -1.603140 | -1.969238 |
| 2.Si  | 1.839769  | -2.056419 | -0.290616 |
| 3.Si  | 1.928672  | 0.058923  | -1.845141 |
| 4.Si  | 2.845125  | -0.004646 | 0.440893  |
| 5.Si  | 1.200189  | -1.296957 | 1.954333  |
| 6.Si  | 1.293546  | 1.227091  | 1.963249  |
| 7.Si  | 1.858746  | 2.069782  | -0.336218 |
| 8.Si  | -1.858746 | -2.069782 | -0.336218 |
| 9.Si  | -1.293546 | -1.227091 | 1.963249  |
| 10.Si | -1.928672 | -0.058923 | -1.845141 |
| 11.Si | -0.082305 | 1.603140  | -1.969238 |
| 12.Si | -2.845125 | 0.004646  | 0.440893  |
| 13.Si | -1.839769 | 2.056419  | -0.290616 |
| 14.Si | -1.200189 | 1.296957  | 1.954333  |
| 15.V  | 0.000000  | 0.000000  | 0.090157  |

C: -77.99298926 eV quartet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.521868  | 1.521868  | 1.521868  |
| 2.Si  | 1.521868  | -1.521868 | 1.521868  |
| 3.Si  | 1.521868  | -1.521868 | -1.521868 |
| 4.Si  | 1.521868  | 1.521868  | -1.521868 |
| 5.Si  | -1.521868 | -1.521868 | -1.521868 |
| 6.Si  | -1.521868 | -1.521868 | 1.521868  |
| 7.Si  | -1.521868 | 1.521868  | 1.521868  |
| 8.Si  | -1.521868 | 1.521868  | -1.521868 |
| 9.Si  | 0.000000  | -2.746822 | 0.000000  |
| 10.Si | 0.000000  | 2.746822  | 0.000000  |
| 11.Si | 2.746822  | 0.000000  | 0.000000  |
| 12.Si | -2.746822 | 0.000000  | 0.000000  |
| 13.Si | 0.000000  | 0.000000  | 2.746822  |
| 14.Si | 0.000000  | 0.000000  | -2.746822 |
| 15.V  | 0.000000  | 0.000000  | 0.000000  |

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Cr@Si<sub>14</sub>

A: -81.18069393 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.146952  | -1.986580 | 1.812217  |
| 2.Si  | 2.322341  | -1.145238 | 0.000000  |
| 3.Si  | -0.169365 | -2.583825 | 0.000000  |
| 4.Si  | 1.146952  | -1.986580 | -1.812217 |
| 5.Si  | 2.322341  | 1.145238  | 0.000000  |
| 6.Si  | 1.146952  | 1.986580  | -1.812217 |
| 7.Si  | 0.000000  | 0.000000  | -2.491400 |
| 8.Si  | 0.000000  | 0.000000  | 2.491400  |
| 9.Si  | 1.146952  | 1.986580  | 1.812217  |
| 10.Si | -2.152976 | -1.438587 | 0.000000  |
| 11.Si | -2.293904 | 0.000000  | -1.812217 |
| 12.Si | -2.293904 | 0.000000  | 1.812217  |
| 13.Si | -2.152976 | 1.438587  | 0.000000  |

|       |           |          |          |
|-------|-----------|----------|----------|
| 14.Si | -0.169365 | 2.583825 | 0.000000 |
| 15.Cr | 0.000000  | 0.000000 | 0.000000 |

B: -80.56701335 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.525440 | -1.985297 |
| 2.Si  | 1.764312  | -2.037840 | -0.308659 |
| 3.Si  | 2.028858  | 0.000000  | -1.843242 |
| 4.Si  | 2.794117  | 0.000000  | 0.477548  |
| 5.Si  | 1.229787  | -1.249764 | 1.957928  |
| 6.Si  | 1.229787  | 1.249764  | 1.957928  |
| 7.Si  | 1.764312  | 2.037840  | -0.308659 |
| 8.Si  | -1.764312 | -2.037840 | -0.308659 |
| 9.Si  | -1.229787 | -1.249764 | 1.957928  |
| 10.Si | -2.028858 | 0.000000  | -1.843242 |
| 11.Si | 0.000000  | 1.525440  | -1.985297 |
| 12.Si | -2.794117 | 0.000000  | 0.477548  |
| 13.Si | -1.764312 | 2.037840  | -0.308659 |
| 14.Si | -1.229787 | 1.249764  | 1.957928  |
| 15.Cr | 0.000000  | 0.000000  | 0.056873  |

C: -80.06775658 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.542969  | 1.546443  | 1.542147  |
| 2.Si  | 1.451444  | -1.436590 | 1.460859  |
| 3.Si  | 1.517816  | -1.509518 | -1.547302 |
| 4.Si  | 1.549442  | 1.527012  | -1.534753 |
| 5.Si  | -1.542969 | -1.546443 | -1.542147 |
| 6.Si  | -1.549442 | -1.527012 | 1.534753  |
| 7.Si  | -1.517816 | 1.509518  | 1.547302  |
| 8.Si  | -1.451444 | 1.436590  | -1.460859 |
| 9.Si  | -0.037607 | -2.704100 | -0.030919 |
| 10.Si | 0.037607  | 2.704100  | 0.030919  |
| 11.Si | 2.725448  | 0.036895  | -0.027470 |
| 12.Si | -2.725448 | -0.036895 | 0.027470  |
| 13.Si | -0.022821 | 0.026354  | 2.741937  |
| 14.Si | 0.022821  | -0.026354 | -2.741937 |
| 15.Cr | 0.000000  | 0.000000  | 0.000000  |

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Mn@Si<sub>14</sub>

A: -81.22347508 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.116548  | -1.924548 | 1.815042  |
| 2.Si  | 2.428690  | -1.215178 | 0.000000  |
| 3.Si  | -0.162711 | -2.717282 | 0.000000  |
| 4.Si  | 1.116548  | -1.924548 | -1.815042 |
| 5.Si  | 2.353923  | 1.112233  | 0.000000  |
| 6.Si  | 1.153337  | 1.999592  | -1.805646 |
| 7.Si  | -0.012245 | 0.075635  | -2.554909 |
| 8.Si  | -0.012245 | 0.075635  | 2.554909  |
| 9.Si  | 1.153337  | 1.999592  | 1.805646  |
| 10.Si | -2.189814 | -1.504397 | 0.000000  |
| 11.Si | -2.276271 | 0.001928  | -1.807925 |
| 12.Si | -2.276271 | 0.001928  | 1.807925  |
| 13.Si | -2.192518 | 1.473562  | 0.000000  |
| 14.Si | -0.193118 | 2.591560  | 0.000000  |
| 15.Mn | -0.003748 | -0.023481 | 0.000000  |

B: -80.62800894 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.469711 | -2.031026 |
| 2.Si  | 1.789228  | -2.068470 | -0.304769 |
| 3.Si  | 2.034286  | 0.000000  | -1.876762 |
| 4.Si  | 2.783041  | 0.000000  | 0.466816  |
| 5.Si  | 1.216387  | -1.243873 | 1.992943  |
| 6.Si  | 1.216387  | 1.243873  | 1.992943  |
| 7.Si  | 1.789228  | 2.068470  | -0.304769 |
| 8.Si  | -1.789228 | -2.068470 | -0.304769 |
| 9.Si  | -1.216387 | -1.243873 | 1.992943  |
| 10.Si | -2.034286 | 0.000000  | -1.876762 |
| 11.Si | 0.000000  | 1.469711  | -2.031026 |
| 12.Si | -2.783041 | 0.000000  | 0.466816  |
| 13.Si | -1.789228 | 2.068470  | -0.304769 |
| 14.Si | -1.216387 | 1.243873  | 1.992943  |
| 15.Mn | 0.000000  | 0.000000  | 0.069393  |

C: -80.36667470 eV doublet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.463106  | 1.507776  | -1.510505 |
| 2.Si  | 1.488919  | -1.493445 | -1.459234 |
| 3.Si  | -1.492895 | -1.456264 | -1.496078 |
| 4.Si  | -1.571345 | 1.581905  | -1.577851 |
| 5.Si  | -1.463106 | -1.507776 | 1.510505  |
| 6.Si  | 1.571345  | -1.581905 | 1.577851  |
| 7.Si  | 1.492895  | 1.456264  | 1.496078  |
| 8.Si  | -1.488919 | 1.493445  | 1.459234  |
| 9.Si  | 0.024469  | -2.711029 | 0.035028  |
| 10.Si | -0.024469 | 2.711029  | -0.035028 |
| 11.Si | -0.029831 | 0.037447  | -2.712611 |
| 12.Si | 0.029831  | -0.037447 | 2.712611  |
| 13.Si | 2.700426  | -0.028135 | 0.026593  |
| 14.Si | -2.700426 | 0.028135  | -0.026593 |
| 15.Mn | 0.000000  | 0.000000  | 0.000000  |

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Fe@Si<sub>14</sub>

A: -80.57339789 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.205254  | -2.087561 | 1.906848  |
| 2.Si  | 2.237007  | -1.175767 | 0.000000  |
| 3.Si  | -0.100259 | -2.525189 | 0.000000  |
| 4.Si  | 1.205254  | -2.087561 | -1.906848 |
| 5.Si  | 2.237007  | 1.175767  | 0.000000  |
| 6.Si  | 1.205254  | 2.087561  | -1.906848 |
| 7.Si  | 0.000000  | 0.000000  | -2.405927 |
| 8.Si  | 0.000000  | 0.000000  | 2.405927  |
| 9.Si  | 1.205254  | 2.087561  | 1.906848  |
| 10.Si | -2.136748 | -1.349422 | 0.000000  |
| 11.Si | -2.410508 | 0.000000  | -1.906848 |
| 12.Si | -2.410508 | 0.000000  | 1.906848  |
| 13.Si | -2.136748 | 1.349422  | 0.000000  |
| 14.Si | -0.100259 | 2.525189  | 0.000000  |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

B: -79.47636866 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.434735 | -2.056898 |
| 2.Si  | 1.714267  | -2.062890 | -0.278908 |
| 3.Si  | 1.983933  | 0.000000  | -1.894391 |
| 4.Si  | 2.700905  | 0.000000  | 0.432849  |
| 5.Si  | 1.183469  | -1.219291 | 2.015298  |
| 6.Si  | 1.183469  | 1.219291  | 2.015298  |
| 7.Si  | 1.714267  | 2.062890  | -0.278908 |
| 8.Si  | -1.714267 | -2.062890 | -0.278908 |
| 9.Si  | -1.183469 | -1.219291 | 2.015298  |
| 10.Si | -1.983933 | 0.000000  | -1.894391 |
| 11.Si | 0.000000  | 1.434735  | -2.056898 |
| 12.Si | -2.700905 | 0.000000  | 0.432849  |
| 13.Si | -1.714267 | 2.062890  | -0.278908 |
| 14.Si | -1.183469 | 1.219291  | 2.015298  |
| 15.Fe | 0.000000  | 0.000000  | 0.050240  |

C: -80.25798713 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.498415  | 1.498415  | 1.498415  |
| 2.Si  | 1.498415  | -1.498415 | 1.498415  |
| 3.Si  | 1.498415  | -1.498415 | -1.498415 |
| 4.Si  | 1.498415  | 1.498415  | -1.498415 |
| 5.Si  | -1.498415 | -1.498415 | -1.498415 |
| 6.Si  | -1.498415 | -1.498415 | 1.498415  |
| 7.Si  | -1.498415 | 1.498415  | 1.498415  |
| 8.Si  | -1.498415 | 1.498415  | -1.498415 |
| 9.Si  | 0.000000  | -2.681049 | 0.000000  |
| 10.Si | 0.000000  | 2.681049  | 0.000000  |
| 11.Si | 2.681049  | 0.000000  | 0.000000  |
| 12.Si | -2.681049 | 0.000000  | 0.000000  |
| 13.Si | 0.000000  | 0.000000  | 2.681049  |
| 14.Si | 0.000000  | 0.000000  | -2.681049 |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

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**Table S4.** Optimised coordinates and total energies for isomers A-C in Figure 2 (d) (PBE)

[Ti@Si<sub>14</sub>]<sup>2-</sup>

A: -78.90842063 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.134281  | -1.964632 | 1.800177  |
| 2.Si  | 2.395280  | -1.165974 | 0.000000  |
| 3.Si  | -0.187877 | -2.657361 | 0.000000  |
| 4.Si  | 1.134281  | -1.964632 | -1.800177 |
| 5.Si  | 2.395280  | 1.165974  | 0.000000  |
| 6.Si  | 1.134281  | 1.964632  | -1.800177 |
| 7.Si  | 0.000000  | 0.000000  | -2.584518 |
| 8.Si  | 0.000000  | 0.000000  | 2.584518  |
| 9.Si  | 1.134281  | 1.964632  | 1.800177  |
| 10.Si | -2.207403 | -1.491387 | 0.000000  |
| 11.Si | -2.268561 | 0.000000  | -1.800177 |
| 12.Si | -2.268561 | 0.000000  | 1.800177  |
| 13.Si | -2.207403 | 1.491387  | 0.000000  |
| 14.Si | -0.187877 | 2.657361  | 0.000000  |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

B: -79.73548107 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.509054 | -2.046998 |
| 2.Si  | 1.795019  | -2.018632 | -0.345482 |
| 3.Si  | 2.067977  | 0.000000  | -1.830739 |
| 4.Si  | 2.814817  | 0.000000  | 0.543037  |
| 5.Si  | 1.258386  | -1.286310 | 1.979599  |
| 6.Si  | 1.258386  | 1.286310  | 1.979599  |
| 7.Si  | 1.795019  | 2.018632  | -0.345482 |
| 8.Si  | -1.795019 | -2.018632 | -0.345482 |
| 9.Si  | -1.258386 | -1.286310 | 1.979599  |
| 10.Si | -2.067977 | 0.000000  | -1.830739 |
| 11.Si | 0.000000  | 1.509054  | -2.046998 |
| 12.Si | -2.814817 | 0.000000  | 0.543037  |
| 13.Si | -1.795019 | 2.018632  | -0.345482 |
| 14.Si | -1.258386 | 1.286310  | 1.979599  |
| 15.Ti | 0.000000  | 0.000000  | 0.072579  |

C: -77.80186413 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.534288  | 1.467869  | 1.530092  |
| 2.Si  | 1.520276  | -1.438774 | 1.515741  |
| 3.Si  | 1.518370  | -1.453853 | -1.524305 |
| 4.Si  | 1.527139  | 1.460167  | -1.518897 |
| 5.Si  | -1.534288 | -1.467869 | -1.530092 |
| 6.Si  | -1.527139 | -1.460167 | 1.518897  |
| 7.Si  | -1.518370 | 1.453853  | 1.524305  |
| 8.Si  | -1.520276 | 1.438774  | -1.515741 |
| 9.Si  | -0.010918 | -2.709839 | -0.008695 |
| 10.Si | 0.010918  | 2.709839  | 0.008695  |
| 11.Si | 2.811334  | 0.010854  | -0.002729 |
| 12.Si | -2.811334 | -0.010854 | 0.002729  |
| 13.Si | 0.001600  | 0.005742  | 2.807641  |
| 14.Si | -0.001600 | -0.005742 | -2.807641 |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

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[V@Si<sub>14</sub>]

A: -77.31113480 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.132776  | -1.962025 | 1.802565  |
| 2.Si  | 2.352596  | -1.155243 | 0.000000  |
| 3.Si  | -0.175828 | -2.615030 | 0.000000  |
| 4.Si  | 1.132776  | -1.962025 | -1.802565 |
| 5.Si  | 2.352596  | 1.155243  | 0.000000  |
| 6.Si  | 1.132776  | 1.962025  | -1.802565 |
| 7.Si  | 0.000000  | 0.000000  | -2.544061 |
| 8.Si  | 0.000000  | 0.000000  | 2.544061  |
| 9.Si  | 1.132776  | 1.962025  | 1.802565  |
| 10.Si | -2.176768 | -1.459787 | 0.000000  |
| 11.Si | -2.265551 | 0.000000  | -1.802565 |
| 12.Si | -2.265551 | 0.000000  | 1.802565  |
| 13.Si | -2.176768 | 1.459787  | 0.000000  |
| 14.Si | -0.175828 | 2.615030  | 0.000000  |
| 15.V  | 0.000000  | 0.000000  | 0.000000  |

B: -77.90008046 eV singlet

|      |          |           |           |
|------|----------|-----------|-----------|
| 1.Si | 0.000000 | -1.506390 | -2.010900 |
| 2.Si | 1.759075 | -2.015274 | -0.329979 |
| 3.Si | 2.030449 | 0.000000  | -1.823342 |
| 4.Si | 2.787661 | 0.000000  | 0.516125  |

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 5.Si  | 1.236834  | -1.264383 | 1.958399  |
| 6.Si  | 1.236834  | 1.264383  | 1.958399  |
| 7.Si  | 1.759075  | 2.015274  | -0.329979 |
| 8.Si  | -1.759075 | -2.015274 | -0.329979 |
| 9.Si  | -1.236834 | -1.264383 | 1.958399  |
| 10.Si | -2.030449 | 0.000000  | -1.823342 |
| 11.Si | 0.000000  | 1.506390  | -2.010900 |
| 12.Si | -2.787661 | 0.000000  | 0.516125  |
| 13.Si | -1.759075 | 2.015274  | -0.329979 |
| 14.Si | -1.236834 | 1.264383  | 1.958399  |
| 15.V  | 0.000000  | 0.000000  | 0.066524  |

C: -76.54671441 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.510392  | 1.503676  | 1.510572  |
| 2.Si  | 1.443228  | -1.422387 | 1.451335  |
| 3.Si  | 1.490035  | -1.477511 | -1.513351 |
| 4.Si  | 1.511109  | 1.489359  | -1.502420 |
| 5.Si  | -1.510392 | -1.503676 | -1.510572 |
| 6.Si  | -1.511109 | -1.489359 | 1.502420  |
| 7.Si  | -1.490035 | 1.477511  | 1.513351  |
| 8.Si  | -1.443228 | 1.422387  | -1.451335 |
| 9.Si  | -0.032636 | -2.731050 | -0.029522 |
| 10.Si | 0.032636  | 2.731050  | 0.029522  |
| 11.Si | 2.756886  | 0.032012  | -0.024699 |
| 12.Si | -2.756886 | -0.032012 | 0.024699  |
| 13.Si | -0.020227 | 0.024994  | 2.768688  |
| 14.Si | 0.020227  | -0.024994 | -2.768688 |
| 15.V  | 0.000000  | 0.000000  | 0.000000  |

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[Mn@Si<sub>14</sub>]<sup>+</sup>

A: -70.42919919 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.118235  | -1.936840 | 1.788909  |
| 2.Si  | 2.329158  | -1.145941 | 0.000000  |
| 3.Si  | -0.172165 | -2.590081 | 0.000000  |
| 4.Si  | 1.118235  | -1.936840 | -1.788909 |
| 5.Si  | 2.329158  | 1.145941  | 0.000000  |
| 6.Si  | 1.118235  | 1.936840  | -1.788909 |
| 7.Si  | 0.000000  | 0.000000  | -2.530950 |
| 8.Si  | 0.000000  | 0.000000  | 2.530950  |
| 9.Si  | 1.118235  | 1.936840  | 1.788909  |
| 10.Si | -2.156993 | -1.444139 | 0.000000  |
| 11.Si | -2.236470 | 0.000000  | -1.788909 |
| 12.Si | -2.236470 | 0.000000  | 1.788909  |
| 13.Si | -2.156993 | 1.444139  | 0.000000  |
| 14.Si | -0.172165 | 2.590081  | 0.000000  |
| 15.Mn | 0.000000  | 0.000000  | 0.000000  |

B: -70.37904128 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.556768 | -1.975128 |
| 2.Si  | 1.719420  | -2.014966 | -0.304776 |
| 3.Si  | 1.934031  | 0.000000  | -1.813933 |
| 4.Si  | 2.760448  | 0.000000  | 0.469250  |
| 5.Si  | 1.218865  | -1.237416 | 1.941640  |
| 6.Si  | 1.218865  | 1.237416  | 1.941640  |
| 7.Si  | 1.719420  | 2.014966  | -0.304776 |
| 8.Si  | -1.719420 | -2.014966 | -0.304776 |
| 9.Si  | -1.218865 | -1.237416 | 1.941640  |
| 10.Si | -1.934031 | 0.000000  | -1.813933 |
| 11.Si | 0.000000  | 1.556768  | -1.975128 |
| 12.Si | -2.760448 | 0.000000  | 0.469250  |
| 13.Si | -1.719420 | 2.014966  | -0.304776 |
| 14.Si | -1.218865 | 1.237416  | 1.941640  |
| 15.Mn | 0.000000  | 0.000000  | 0.050527  |

C: -69.89719676 eV triplet

|      |           |           |           |
|------|-----------|-----------|-----------|
| 1.Si | 1.528406  | 1.482955  | 1.527635  |
| 2.Si | 1.437422  | -1.426678 | 1.437322  |
| 3.Si | 1.522007  | -1.514939 | -1.490013 |
| 4.Si | 1.487481  | 1.519449  | -1.525077 |
| 5.Si | -1.528406 | -1.482955 | -1.527635 |
| 6.Si | -1.487481 | -1.519449 | 1.525077  |
| 7.Si | -1.522007 | 1.514939  | 1.490013  |
| 8.Si | -1.437422 | 1.426678  | -1.437322 |
| 9.Si | -0.053521 | -2.667972 | -0.053527 |

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 10.Si | 0.053521  | 2.667972  | 0.053527  |
| 11.Si | 2.683708  | 0.052788  | -0.052998 |
| 12.Si | -2.683708 | -0.052788 | 0.052998  |
| 13.Si | -0.048440 | 0.049895  | 2.688718  |
| 14.Si | 0.048440  | -0.049895 | -2.688718 |
| 15.Mn | 0.000000  | 0.000000  | 0.000000  |

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[Fe@Si<sub>14</sub>]<sup>2+</sup>

A: -65.51167875 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.102852  | -1.910195 | 1.767505  |
| 2.Si  | 2.347732  | -1.146322 | 0.000000  |
| 3.Si  | -0.181121 | -2.606357 | 0.000000  |
| 4.Si  | 1.102852  | -1.910195 | -1.767505 |
| 5.Si  | 2.347732  | 1.146322  | 0.000000  |
| 6.Si  | 1.102852  | 1.910195  | -1.767505 |
| 7.Si  | 0.000000  | 0.000000  | -2.589497 |
| 8.Si  | 0.000000  | 0.000000  | 2.589497  |
| 9.Si  | 1.102852  | 1.910195  | 1.767505  |
| 10.Si | -2.166610 | -1.460034 | 0.000000  |
| 11.Si | -2.205704 | 0.000000  | -1.767505 |
| 12.Si | -2.205704 | 0.000000  | 1.767505  |
| 13.Si | -2.166610 | 1.460034  | 0.000000  |
| 14.Si | -0.181121 | 2.606357  | 0.000000  |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

B: -65.08806737 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.622384 | -1.972107 |
| 2.Si  | 1.712460  | -2.017656 | -0.293139 |
| 3.Si  | 1.862111  | 0.000000  | -1.810978 |
| 4.Si  | 2.763535  | 0.000000  | 0.438285  |
| 5.Si  | 1.217780  | -1.228087 | 1.945180  |
| 6.Si  | 1.217780  | 1.228087  | 1.945180  |
| 7.Si  | 1.712460  | 2.017656  | -0.293139 |
| 8.Si  | -1.712460 | -2.017656 | -0.293139 |
| 9.Si  | -1.217780 | -1.228087 | 1.945180  |
| 10.Si | -1.862111 | 0.000000  | -1.810978 |
| 11.Si | 0.000000  | 1.622384  | -1.972107 |
| 12.Si | -2.763535 | 0.000000  | 0.438285  |
| 13.Si | -1.712460 | 2.017656  | -0.293139 |
| 14.Si | -1.217780 | 1.228087  | 1.945180  |
| 15.Fe | 0.000000  | 0.000000  | 0.045159  |

C: -64.83332843 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.530340  | 1.464664  | 1.530438  |
| 2.Si  | 1.446521  | -1.438266 | 1.446308  |
| 3.Si  | 1.528207  | -1.525462 | -1.473171 |
| 4.Si  | 1.469881  | 1.528025  | -1.530907 |
| 5.Si  | -1.530340 | -1.464664 | -1.530438 |
| 6.Si  | -1.469881 | -1.528025 | 1.530907  |
| 7.Si  | -1.528207 | 1.525462  | 1.473171  |
| 8.Si  | -1.446521 | 1.438266  | -1.446308 |
| 9.Si  | -0.063884 | -2.656470 | -0.065219 |
| 10.Si | 0.063884  | 2.656470  | 0.065219  |
| 11.Si | 2.667132  | 0.063531  | -0.066939 |
| 12.Si | -2.667132 | -0.063531 | 0.066939  |
| 13.Si | -0.062132 | 0.060932  | 2.670294  |
| 14.Si | 0.062132  | -0.060932 | -2.670294 |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

**Table S5.** Optimised coordinates and total energies for isomers A-C in Figure 2 (e) (BLYP)

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[Ti@Si<sub>14</sub>]<sup>2+</sup>

A: -68.14787241 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.163227  | -2.014769 | 1.830493  |
| 2.Si  | 2.419377  | -1.180112 | 0.000000  |
| 3.Si  | -0.187682 | -2.685298 | 0.000000  |
| 4.Si  | 1.163227  | -2.014769 | -1.830493 |
| 5.Si  | 2.419377  | 1.180112  | 0.000000  |
| 6.Si  | 1.163227  | 2.014769  | -1.830493 |
| 7.Si  | 0.000000  | 0.000000  | -2.608248 |
| 8.Si  | 0.000000  | 0.000000  | 2.608248  |
| 9.Si  | 1.163227  | 2.014769  | 1.830493  |
| 10.Si | -2.231695 | -1.505186 | 0.000000  |

|       |           |          |           |
|-------|-----------|----------|-----------|
| 11.Si | -2.326455 | 0.000000 | -1.830493 |
| 12.Si | -2.326455 | 0.000000 | 1.830493  |
| 13.Si | -2.231695 | 1.505186 | 0.000000  |
| 14.Si | -0.187682 | 2.685298 | 0.000000  |
| 15.Ti | 0.000000  | 0.000000 | 0.000000  |

B: -68.30508057 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.570075 | -2.055011 |
| 2.Si  | 1.852724  | -2.045121 | -0.350150 |
| 3.Si  | 2.110680  | 0.000000  | -1.870724 |
| 4.Si  | 2.884499  | 0.000000  | 0.543012  |
| 5.Si  | 1.285387  | -1.307841 | 2.007620  |
| 6.Si  | 1.285387  | 1.307841  | 2.007620  |
| 7.Si  | 1.852724  | 2.045121  | -0.350150 |
| 8.Si  | -1.852724 | -2.045121 | -0.350150 |
| 9.Si  | -1.285387 | -1.307841 | 2.007620  |
| 10.Si | -2.110680 | 0.000000  | -1.870724 |
| 11.Si | 0.000000  | 1.570075  | -2.055011 |
| 12.Si | -2.884499 | 0.000000  | 0.543012  |
| 13.Si | -1.852724 | 2.045121  | -0.350150 |
| 14.Si | -1.285387 | 1.307841  | 2.007620  |
| 15.Ti | 0.000000  | 0.000000  | 0.074118  |

C: -66.36443091 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.554884  | 1.567808  | 1.551153  |
| 2.Si  | 1.485023  | -1.455671 | 1.501751  |
| 3.Si  | 1.520905  | -1.506253 | -1.578826 |
| 4.Si  | 1.578317  | 1.528742  | -1.539708 |
| 5.Si  | -1.554884 | -1.567808 | -1.551153 |
| 6.Si  | -1.578317 | -1.528742 | 1.539708  |
| 7.Si  | -1.520905 | 1.506253  | 1.578826  |
| 8.Si  | -1.485023 | 1.455671  | -1.501751 |
| 9.Si  | -0.032048 | -2.796636 | -0.025414 |
| 10.Si | 0.032048  | 2.796636  | 0.025414  |
| 11.Si | 2.824168  | 0.030135  | -0.018504 |
| 12.Si | -2.824168 | -0.030135 | 0.018504  |
| 13.Si | -0.013799 | 0.019847  | 2.838615  |
| 14.Si | 0.013799  | -0.019847 | -2.838615 |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

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[V@Si<sub>14</sub>]

A: -66.67800905 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.154350  | -1.999393 | 1.821206  |
| 2.Si  | 2.387702  | -1.168406 | 0.000000  |
| 3.Si  | -0.181982 | -2.652014 | 0.000000  |
| 4.Si  | 1.154350  | -1.999393 | -1.821206 |
| 5.Si  | 2.387702  | 1.168406  | 0.000000  |
| 6.Si  | 1.154350  | 1.999393  | -1.821206 |
| 7.Si  | 0.000000  | 0.000000  | -2.570048 |
| 8.Si  | 0.000000  | 0.000000  | 2.570048  |
| 9.Si  | 1.154350  | 1.999393  | 1.821206  |
| 10.Si | -2.205720 | -1.483608 | 0.000000  |
| 11.Si | -2.308700 | 0.000000  | -1.821206 |
| 12.Si | -2.308700 | 0.000000  | 1.821206  |
| 13.Si | -2.205720 | 1.483608  | 0.000000  |
| 14.Si | -0.181982 | 2.652014  | 0.000000  |
| 15.V  | 0.000000  | 0.000000  | 0.000000  |

B: -66.54170266 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.568225 | -2.014576 |
| 2.Si  | 1.813854  | -2.044459 | -0.331385 |
| 3.Si  | 2.068150  | 0.000000  | -1.864320 |
| 4.Si  | 2.852533  | 0.000000  | 0.509580  |
| 5.Si  | 1.259808  | -1.282713 | 1.985123  |
| 6.Si  | 1.259808  | 1.282713  | 1.985123  |
| 7.Si  | 1.813854  | 2.044459  | -0.331385 |
| 8.Si  | -1.813854 | -2.044459 | -0.331385 |
| 9.Si  | -1.259808 | -1.282713 | 1.985123  |
| 10.Si | -2.068150 | 0.000000  | -1.864320 |
| 11.Si | 0.000000  | 1.568225  | -2.014576 |
| 12.Si | -2.852533 | 0.000000  | 0.509580  |
| 13.Si | -1.813854 | 2.044459  | -0.331385 |
| 14.Si | -1.259808 | 1.282713  | 1.985123  |
| 15.V  | 0.000000  | 0.000000  | 0.067142  |

C: -65.20729544 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.539904  | 1.543852  | 1.536502  |
| 2.Si  | 1.462819  | -1.444462 | 1.475293  |
| 3.Si  | 1.514193  | -1.504852 | -1.549590 |
| 4.Si  | 1.550070  | 1.523191  | -1.529463 |
| 5.Si  | -1.539904 | -1.543852 | -1.536502 |
| 6.Si  | -1.550070 | -1.523191 | 1.529463  |
| 7.Si  | -1.514193 | 1.504852  | 1.549590  |
| 8.Si  | -1.462819 | 1.444462  | -1.475293 |
| 9.Si  | -0.036704 | -2.771835 | -0.031853 |
| 10.Si | 0.036704  | 2.771835  | 0.031853  |
| 11.Si | 2.792301  | 0.035828  | -0.028364 |
| 12.Si | -2.792301 | -0.035828 | 0.028364  |
| 13.Si | -0.023335 | 0.026702  | 2.807121  |
| 14.Si | 0.023335  | -0.026702 | -2.807121 |
| 15.V  | 0.000000  | 0.000000  | 0.000000  |

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[Mn@Si<sub>14</sub>]<sup>+</sup>

A: -60.39852685 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.138176  | -1.971378 | 1.802086  |
| 2.Si  | 2.369136  | -1.158861 | 0.000000  |
| 3.Si  | -0.180964 | -2.631163 | 0.000000  |
| 4.Si  | 1.138176  | -1.971378 | -1.802086 |
| 5.Si  | 2.369136  | 1.158861  | 0.000000  |
| 6.Si  | 1.138176  | 1.971378  | -1.802086 |
| 7.Si  | 0.000000  | 0.000000  | -2.557375 |
| 8.Si  | 0.000000  | 0.000000  | 2.557375  |
| 9.Si  | 1.138176  | 1.971378  | 1.802086  |
| 10.Si | -2.188171 | -1.472301 | 0.000000  |
| 11.Si | -2.276352 | 0.000000  | -1.802086 |
| 12.Si | -2.276352 | 0.000000  | 1.802086  |
| 13.Si | -2.188171 | 1.472301  | 0.000000  |
| 14.Si | -0.180964 | 2.631163  | 0.000000  |
| 15.Mn | 0.000000  | 0.000000  | 0.000000  |

B: -59.54895239 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.608167 | -1.970362 |
| 2.Si  | 1.781365  | -2.047666 | -0.305464 |
| 3.Si  | 1.980901  | 0.000000  | -1.860534 |
| 4.Si  | 2.817740  | 0.000000  | 0.457233  |
| 5.Si  | 1.238121  | -1.254853 | 1.967706  |
| 6.Si  | 1.238121  | 1.254853  | 1.967706  |
| 7.Si  | 1.781365  | 2.047666  | -0.305464 |
| 8.Si  | -1.781365 | -2.047666 | -0.305464 |
| 9.Si  | -1.238121 | -1.254853 | 1.967706  |
| 10.Si | -1.980901 | 0.000000  | -1.860534 |
| 11.Si | 0.000000  | 1.608167  | -1.970362 |
| 12.Si | -2.817740 | 0.000000  | 0.457233  |
| 13.Si | -1.781365 | 2.047666  | -0.305464 |
| 14.Si | -1.238121 | 1.254853  | 1.967706  |
| 15.Mn | 0.000000  | 0.000000  | 0.053679  |

C: -59.08329091 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.590354  | 1.559291  | 1.591854  |
| 2.Si  | 1.478590  | -1.470650 | 1.484913  |
| 3.Si  | 1.576837  | -1.574093 | -1.563376 |
| 4.Si  | 1.560798  | 1.584067  | -1.589988 |
| 5.Si  | -1.590354 | -1.559291 | -1.591854 |
| 6.Si  | -1.560798 | -1.584067 | 1.589988  |
| 7.Si  | -1.576837 | 1.574093  | 1.563376  |
| 8.Si  | -1.478590 | 1.470650  | -1.484913 |
| 9.Si  | -0.051937 | -2.659522 | -0.051791 |
| 10.Si | 0.051937  | 2.659522  | 0.051791  |
| 11.Si | 2.671237  | 0.051661  | -0.050266 |
| 12.Si | -2.671237 | -0.051661 | 0.050266  |
| 13.Si | -0.046560 | 0.047169  | 2.685124  |
| 14.Si | 0.046560  | -0.047169 | -2.685124 |
| 15.Mn | 0.000000  | 0.000000  | 0.000000  |

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[Fe@Si<sub>14</sub>]<sup>2+</sup>

A: -55.90682679 eV singlet

|      |          |           |          |
|------|----------|-----------|----------|
| 1.Si | 1.121827 | -1.943061 | 1.780686 |
|------|----------|-----------|----------|



|       |           |           |           |
|-------|-----------|-----------|-----------|
| 2.Si  | 2.392732  | -1.162699 | 0.000000  |
| 3.Si  | -0.189439 | -2.653516 | 0.000000  |
| 4.Si  | 1.121827  | -1.943061 | -1.780686 |
| 5.Si  | 2.392732  | 1.162699  | 0.000000  |
| 6.Si  | 1.121827  | 1.943061  | -1.780686 |
| 7.Si  | 0.000000  | 0.000000  | -2.605530 |
| 8.Si  | 0.000000  | 0.000000  | 2.605530  |
| 9.Si  | 1.121827  | 1.943061  | 1.780686  |
| 10.Si | -2.203293 | -1.490817 | 0.000000  |
| 11.Si | -2.243654 | 0.000000  | -1.780686 |
| 12.Si | -2.243654 | 0.000000  | 1.780686  |
| 13.Si | -2.203293 | 1.490817  | 0.000000  |
| 14.Si | -0.189439 | 2.653516  | 0.000000  |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

B: -54.67129138 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.676810 | -1.967344 |
| 2.Si  | 1.770754  | -2.054630 | -0.292899 |
| 3.Si  | 1.904558  | 0.000000  | -1.859332 |
| 4.Si  | 2.816866  | 0.000000  | 0.423333  |
| 5.Si  | 1.236098  | -1.246450 | 1.972069  |
| 6.Si  | 1.236098  | 1.246450  | 1.972069  |
| 7.Si  | 1.770754  | 2.054630  | -0.292899 |
| 8.Si  | -1.770754 | -2.054630 | -0.292899 |
| 9.Si  | -1.236098 | -1.246450 | 1.972069  |
| 10.Si | -1.904558 | 0.000000  | -1.859332 |
| 11.Si | 0.000000  | 1.676810  | -1.967344 |
| 12.Si | -2.816866 | 0.000000  | 0.423333  |
| 13.Si | -1.770754 | 2.054630  | -0.292899 |
| 14.Si | -1.236098 | 1.246450  | 1.972069  |
| 15.Fe | 0.000000  | 0.000000  | 0.049446  |

C: -54.43450779 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.649126  | 1.537956  | 1.647013  |
| 2.Si  | 1.485609  | -1.481632 | 1.482544  |
| 3.Si  | 1.646936  | -1.646741 | -1.542324 |
| 4.Si  | 1.538085  | 1.646871  | -1.646342 |
| 5.Si  | -1.649126 | -1.537956 | -1.647013 |
| 6.Si  | -1.538085 | -1.646871 | 1.646342  |
| 7.Si  | -1.646936 | 1.646741  | 1.542324  |
| 8.Si  | -1.485609 | 1.481632  | -1.482544 |
| 9.Si  | -0.098609 | -2.607635 | -0.100719 |
| 10.Si | 0.098609  | 2.607635  | 0.100719  |
| 11.Si | 2.613706  | 0.098864  | -0.100135 |
| 12.Si | -2.613706 | -0.098864 | 0.100135  |
| 13.Si | -0.096535 | 0.096958  | 2.610354  |
| 14.Si | 0.096535  | -0.096958 | -2.610354 |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

**Table S6.** Optimised coordinates and total energies for isomers A-C in Figure 2 (f) (B3LYP)

[Ti@Si<sub>14</sub>]<sup>2-</sup>

A: -84.08936963 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.156376  | -2.002902 | 1.817682  |
| 2.Si  | 2.393614  | -1.161083 | 0.000000  |
| 3.Si  | -0.191280 | -2.653472 | 0.000000  |
| 4.Si  | 1.156376  | -2.002902 | -1.817682 |
| 5.Si  | 2.393614  | 1.161083  | 0.000000  |
| 6.Si  | 1.156376  | 2.002902  | -1.817682 |
| 7.Si  | 0.000000  | 0.000000  | -2.581927 |
| 8.Si  | 0.000000  | 0.000000  | 2.581927  |
| 9.Si  | 1.156376  | 2.002902  | 1.817682  |
| 10.Si | -2.202334 | -1.492389 | 0.000000  |
| 11.Si | -2.312752 | 0.000000  | -1.817682 |
| 12.Si | -2.312752 | 0.000000  | 1.817682  |
| 13.Si | -2.202334 | 1.492389  | 0.000000  |
| 14.Si | -0.191280 | 2.653472  | 0.000000  |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

B: -84.23730147 eV singlet

|      |          |           |           |
|------|----------|-----------|-----------|
| 1.Si | 0.000000 | -1.516486 | -2.056471 |
| 2.Si | 1.824522 | -2.031999 | -0.347158 |

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 3.Si  | 2.112261  | 0.000000  | -1.843178 |
| 4.Si  | 2.852198  | 0.000000  | 0.539381  |
| 5.Si  | 1.274063  | -1.297248 | 1.991312  |
| 6.Si  | 1.274063  | 1.297248  | 1.991312  |
| 7.Si  | 1.824522  | 2.031999  | -0.347158 |
| 8.Si  | -1.824522 | -2.031999 | -0.347158 |
| 9.Si  | -1.274063 | -1.297248 | 1.991312  |
| 10.Si | -2.112261 | 0.000000  | -1.843178 |
| 11.Si | 0.000000  | 1.516486  | -2.056471 |
| 12.Si | -2.852198 | 0.000000  | 0.539381  |
| 13.Si | -1.824522 | 2.031999  | -0.347158 |
| 14.Si | -1.274063 | 1.297248  | 1.991312  |
| 15.Ti | 0.000000  | 0.000000  | 0.078992  |

C: -82.07551341 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.535024  | 1.553356  | 1.532226  |
| 2.Si  | 1.465941  | -1.438843 | 1.482043  |
| 3.Si  | 1.501798  | -1.489318 | -1.563330 |
| 4.Si  | 1.561629  | 1.510572  | -1.520203 |
| 5.Si  | -1.535024 | -1.553356 | -1.532226 |
| 6.Si  | -1.561629 | -1.510572 | 1.520203  |
| 7.Si  | -1.501798 | 1.489318  | 1.563330  |
| 8.Si  | -1.465941 | 1.438843  | -1.482043 |
| 9.Si  | -0.030892 | -2.785132 | -0.024598 |
| 10.Si | 0.030892  | 2.785132  | 0.024598  |
| 11.Si | 2.810032  | 0.029085  | -0.017221 |
| 12.Si | -2.810032 | -0.029085 | 0.017221  |
| 13.Si | -0.012805 | 0.019543  | 2.824338  |
| 14.Si | 0.012805  | -0.019543 | -2.824338 |
| 15.Ti | 0.000000  | 0.000000  | 0.000000  |

[V@Si<sub>14</sub>]

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A: -83.12958089 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.148366  | -1.989027 | 1.811693  |
| 2.Si  | 2.354496  | -1.150382 | 0.000000  |
| 3.Si  | -0.180987 | -2.614244 | 0.000000  |
| 4.Si  | 1.148366  | -1.989027 | -1.811693 |
| 5.Si  | 2.354496  | 1.150382  | 0.000000  |
| 6.Si  | 1.148366  | 1.989027  | -1.811693 |
| 7.Si  | 0.000000  | 0.000000  | -2.532623 |
| 8.Si  | 0.000000  | 0.000000  | 2.532623  |
| 9.Si  | 1.148366  | 1.989027  | 1.811693  |
| 10.Si | -2.173508 | -1.463862 | 0.000000  |
| 11.Si | -2.296731 | 0.000000  | -1.811693 |
| 12.Si | -2.296731 | 0.000000  | 1.811693  |
| 13.Si | -2.173508 | 1.463862  | 0.000000  |
| 14.Si | -0.180987 | 2.614244  | 0.000000  |
| 15.V  | 0.000000  | 0.000000  | 0.000000  |

B: -82.93141235 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.510720 | -2.011878 |
| 2.Si  | 1.788361  | -2.030160 | -0.327614 |
| 3.Si  | 2.072531  | 0.000000  | -1.840758 |
| 4.Si  | 2.822521  | 0.000000  | 0.504882  |
| 5.Si  | 1.248403  | -1.267544 | 1.968650  |
| 6.Si  | 1.248403  | 1.267544  | 1.968650  |
| 7.Si  | 1.788361  | 2.030160  | -0.327614 |
| 8.Si  | -1.788361 | -2.030160 | -0.327614 |
| 9.Si  | -1.248403 | -1.267544 | 1.968650  |
| 10.Si | -2.072531 | 0.000000  | -1.840758 |
| 11.Si | 0.000000  | 1.510720  | -2.011878 |
| 12.Si | -2.822521 | 0.000000  | 0.504882  |
| 13.Si | -1.788361 | 2.030160  | -0.327614 |
| 14.Si | -1.248403 | 1.267544  | 1.968650  |
| 15.V  | 0.000000  | 0.000000  | 0.071361  |

C: -81.63843972 eV triplet

|      |           |           |           |
|------|-----------|-----------|-----------|
| 1.Si | 1.517377  | 1.534652  | 1.518747  |
| 2.Si | 1.442899  | -1.434485 | 1.453943  |
| 3.Si | 1.497157  | -1.493155 | -1.538299 |
| 4.Si | 1.535934  | 1.507941  | -1.513805 |
| 5.Si | -1.517377 | -1.534652 | -1.518747 |
| 6.Si | -1.535934 | -1.507941 | 1.513805  |
| 7.Si | -1.497157 | 1.493155  | 1.538299  |

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 8.Si  | -1.442899 | 1.434485  | -1.453943 |
| 9.Si  | -0.031677 | -2.765002 | -0.027478 |
| 10.Si | 0.031677  | 2.765002  | 0.027478  |
| 11.Si | 2.775322  | 0.031964  | -0.025582 |
| 12.Si | -2.775322 | -0.031964 | 0.025582  |
| 13.Si | -0.021025 | 0.023880  | 2.790135  |
| 14.Si | 0.021025  | -0.023880 | -2.790135 |
| 15.V  | 0.000000  | 0.000000  | 0.000000  |

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[Mn@Si<sub>14</sub>]<sup>+</sup>

A: -77.18862072 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.128264  | -1.954211 | 1.787525  |
| 2.Si  | 2.338465  | -1.142082 | 0.000000  |
| 3.Si  | -0.180160 | -2.596211 | 0.000000  |
| 4.Si  | 1.128264  | -1.954211 | -1.787525 |
| 5.Si  | 2.338465  | 1.142082  | 0.000000  |
| 6.Si  | 1.128264  | 1.954211  | -1.787525 |
| 7.Si  | 0.000000  | 0.000000  | -2.523710 |
| 8.Si  | 0.000000  | 0.000000  | 2.523710  |
| 9.Si  | 1.128264  | 1.954211  | 1.787525  |
| 10.Si | -2.158305 | -1.454129 | 0.000000  |
| 11.Si | -2.256528 | 0.000000  | -1.787525 |
| 12.Si | -2.256528 | 0.000000  | 1.787525  |
| 13.Si | -2.158305 | 1.454129  | 0.000000  |
| 14.Si | -0.180160 | 2.596211  | 0.000000  |
| 15.Mn | 0.000000  | 0.000000  | 0.000000  |

B: -76.17928509 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.570131 | -1.954072 |
| 2.Si  | 1.760345  | -2.040791 | -0.293531 |
| 3.Si  | 1.963789  | 0.000000  | -1.846491 |
| 4.Si  | 2.788761  | 0.000000  | 0.441741  |
| 5.Si  | 1.224196  | -1.235447 | 1.950099  |
| 6.Si  | 1.224196  | 1.235447  | 1.950099  |
| 7.Si  | 1.760345  | 2.040791  | -0.293531 |
| 8.Si  | -1.760345 | -2.040791 | -0.293531 |
| 9.Si  | -1.224196 | -1.235447 | 1.950099  |
| 10.Si | -1.963789 | 0.000000  | -1.846491 |
| 11.Si | 0.000000  | 1.570131  | -1.954072 |
| 12.Si | -2.788761 | 0.000000  | 0.441741  |
| 13.Si | -1.760345 | 2.040791  | -0.293531 |
| 14.Si | -1.224196 | 1.235447  | 1.950099  |
| 15.Mn | 0.000000  | 0.000000  | 0.050120  |

C: -76.41059502 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.573993  | 1.566568  | 1.574705  |
| 2.Si  | 1.473770  | -1.469268 | 1.475954  |
| 3.Si  | 1.564524  | -1.562133 | -1.568450 |
| 4.Si  | 1.566565  | 1.568643  | -1.573386 |
| 5.Si  | -1.573993 | -1.566568 | -1.574705 |
| 6.Si  | -1.566565 | -1.568643 | 1.573386  |
| 7.Si  | -1.564524 | 1.562133  | 1.568450  |
| 8.Si  | -1.473770 | 1.469268  | -1.475954 |
| 9.Si  | -0.039509 | -2.659164 | -0.039106 |
| 10.Si | 0.039509  | 2.659164  | 0.039106  |
| 11.Si | 2.666958  | 0.039853  | -0.037985 |
| 12.Si | -2.666958 | -0.039853 | 0.037985  |
| 13.Si | -0.034063 | 0.034916  | 2.675222  |
| 14.Si | 0.034063  | -0.034916 | -2.675222 |
| 15.Mn | 0.000000  | 0.000000  | 0.000000  |

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[Fe@Si<sub>14</sub>]<sup>2+</sup>

A: -72.68666328 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.108382  | -1.919773 | 1.758753  |
| 2.Si  | 2.363716  | -1.142930 | 0.000000  |
| 3.Si  | -0.192052 | -2.618503 | 0.000000  |
| 4.Si  | 1.108382  | -1.919773 | -1.758753 |
| 5.Si  | 2.363716  | 1.142930  | 0.000000  |
| 6.Si  | 1.108382  | 1.919773  | -1.758753 |
| 7.Si  | 0.000000  | 0.000000  | -2.589395 |
| 8.Si  | 0.000000  | 0.000000  | 2.589395  |
| 9.Si  | 1.108382  | 1.919773  | 1.758753  |
| 10.Si | -2.171664 | -1.475573 | 0.000000  |
| 11.Si | -2.216763 | 0.000000  | -1.758753 |

|       |           |          |          |
|-------|-----------|----------|----------|
| 12.Si | -2.216763 | 0.000000 | 1.758753 |
| 13.Si | -2.171664 | 1.475573 | 0.000000 |
| 14.Si | -0.192052 | 2.618503 | 0.000000 |
| 15.Fe | 0.000000  | 0.000000 | 0.000000 |

B: -71.11336889 eV singlet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 0.000000  | -1.650989 | -1.952883 |
| 2.Si  | 1.750300  | -2.042779 | -0.279879 |
| 3.Si  | 1.868483  | 0.000000  | -1.837794 |
| 4.Si  | 2.789607  | 0.000000  | 0.405383  |
| 5.Si  | 1.220343  | -1.229179 | 1.951603  |
| 6.Si  | 1.220343  | 1.229179  | 1.951603  |
| 7.Si  | 1.750300  | 2.042779  | -0.279879 |
| 8.Si  | -1.750300 | -2.042779 | -0.279879 |
| 9.Si  | -1.220343 | -1.229179 | 1.951603  |
| 10.Si | -1.868483 | 0.000000  | -1.837794 |
| 11.Si | 0.000000  | 1.650989  | -1.952883 |
| 12.Si | -2.789607 | 0.000000  | 0.405383  |
| 13.Si | -1.750300 | 2.042779  | -0.279879 |
| 14.Si | -1.220343 | 1.229179  | 1.951603  |
| 15.Fe | 0.000000  | 0.000000  | 0.046287  |

C: -71.66074997 eV triplet

|       |           |           |           |
|-------|-----------|-----------|-----------|
| 1.Si  | 1.643858  | 1.558161  | 1.640830  |
| 2.Si  | 1.485809  | -1.484098 | 1.483133  |
| 3.Si  | 1.641457  | -1.639304 | -1.561412 |
| 4.Si  | 1.559560  | 1.641794  | -1.642310 |
| 5.Si  | -1.643858 | -1.558161 | -1.640830 |
| 6.Si  | -1.559560 | -1.641794 | 1.642310  |
| 7.Si  | -1.641457 | 1.639304  | 1.561412  |
| 8.Si  | -1.485809 | 1.484098  | -1.483133 |
| 9.Si  | -0.080721 | -2.578447 | -0.081801 |
| 10.Si | 0.080721  | 2.578447  | 0.081801  |
| 11.Si | 2.583785  | 0.081700  | -0.082237 |
| 12.Si | -2.583785 | -0.081700 | 0.082237  |
| 13.Si | -0.078402 | 0.078544  | 2.580401  |
| 14.Si | 0.078402  | -0.078544 | -2.580401 |
| 15.Fe | 0.000000  | 0.000000  | 0.000000  |

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