Supplementary Information for:  
  
Associative vs. dissociative binding of CO2 on M5 transition metal clusters

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|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **r(CO)** | **r(CO)** | **theta(OCO)** | **v\_bend** | **v\_bend** | **v\_symm\_stretch** | **v\_asym\_stretch** | **v\_imag** | **E(HOMO)** | **E(LUMO)** | **q(M5)** | **q(CO2)** | **E\_ads** | **E\_int** |
| **M5** |  |  |  |  |  |  |  |  | -0.16666 | -0.10465 |  |  |  |  |
| **g1** | 1.182 | 1.193 | 179.96 | 553.5658 | 576.876 | 1276.5886 | 2340.6443 |  | -0.15919 | -0.10033 | -0.142 | 0.142 | -0.483 | -0.484 |
| **ts1** | 1.222 | 1.327 | 132.17 | 371.7307 | 709.0994 | 1109.5649 | 1726.4537 | -56.8589 | -0.18717 | -0.13278 | 0.418 | -0.418 | -0.573 | 1.212 |
| **g2** | 1.282 | 1.312 | 132.67 | 482.3571 | 707.4356 | 1132.4489 | 1541.25 |  | -0.18243 | -0.11599 | 0.497 | -0.497 | -2.463 | -0.444 |
| **ts2** | 1.266 | 1.372 | 127.19 | 466.8703 | 697.0335 | 994.0995 | 1516.0432 | -66.7277 | -0.19401 | -0.1161 | 0.590 | -0.590 | -2.199 | 0.207 |
| **g3** | 1.39 | 1.404 | 116.34 | 567.5587 | 626.4673 | 988.4696 | 1056.6941 |  | -0.18108 | -0.11851 | 0.641 | -0.641 | -3.003 | 1.152 |
| **ts3** | 1.7 | 4.173 | 72.92 | 485.3839 | 607.3202 | 631.4852 | 716.5344 | -366.073 | -0.17221 | -0.11299 | 1.050 | -1.050 | -2.215 | 10.438 |
| **g4** | 1.284 | 3.396 | 92.93 | 490.2889 | 611.4769 | 887.3325 | 1398.5032 |  | -0.19439 | -0.12701 | 0.785 | -0.785 | -2.654 | 5.156 |
| **ts4** | 1.7 | 4.173 | 72.92 | 485.3839 | 607.3202 | 631.4852 | 716.5344 | -330.7486 | -0.17221 | -0.11299 | 1.050 | -1.050 | -4.069 | 8.584 |
| **g5** | 2.77 | 3.657 | 68.78 | 600.4482 | 671.546 | 672.5742 | 700.7793 |  | -0.16848 | -0.11514 | 1.273 | -1.273 | -6.778 | 12.486 |
| **ts3b** | 1.296 | 1.692 | 121.26 | 462.646 | 558.8128 | 609.9728 | 1359.8563 | -335.632 | -0.17902 | -0.12054 | 0.649 | -0.649 | -2.087 | 2.925 |
| **g4b** | 1.34 | 3.595 | 122.14 | 500.2116 | 623.6668 | 673.7944 | 1215.8452 |  | -0.17605 | -0.11575 | 0.926 | -0.926 | -4.436 | 4.131 |
| **ts4b** | 1.89 | 3.468 | 77.67 | 566.1126 | 653.6813 | 696.8263 | 747.1924 | -475.5851 | -0.18228 | -0.1154 | 1.008 | -1.008 | -3.928 | 10.280 |
| **g5b** | 3.39 | 3.925 | 81.83 | 602.9637 | 682.8957 | 764.5902 | 901.6891 |  | -0.18045 | -0.12197 | 1.259 | -1.259 | -6.052 | 14.262 |
| **ts5b** | 3.08 | 3.576 | 83.78 | 639.53 | 681.5477 | 720.697 | 866.314 | -140.1948 | -0.17016 | -0.11666 | 1.243 | -1.243 | -6.013 | 13.851 |
| **g6b** | 2.937 | 3.352 | 108.55 | 613.392 | 678.0525 | 679.9405 | 692.9518 |  | -0.16939 | -0.11563 | 1.251 | -1.251 | -6.680 | 13.270 |
| **ts6b** | 2.93 | 2.882 | 89.5 | 595.9234 | 647.5031 | 682.4822 | 690.1 | -64.74 | -0.16584 | -0.10944 | 1.265 | -1.265 | -5.600 | 13.704 |

Table S1. Reaction path data for Nb5 + CO2.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **r(CO)** | **r(CO)** | **theta(OCO)** | **v\_bend** | **v\_bend** | **v\_symm\_stretch** | **v\_asym\_stretch** | **v\_imag** | **E(HOMO)** | **E(LUMO)** | **q(M5)** | **q(CO2)** | **E\_ads** | **E\_int** |
| **M5** |  |  |  |  |  |  |  |  | -0.16899 | -0.09599 |  |  |  |  |
| **g1** | 1.184 | 1.19 | 179.98 | 560.1485 | 560.2182 | 1279.386 | 2339.9683 |  | -0.16124 | -0.08841 | -0.119 | 0.118 | -0.438 | -0.439 |
| **ts1** | 1.191 | 1.8 | 122.03 | 441.9316 | 508.0624 | 767.2144 | 1888.4601 | -355.913 | -0.1877 | -0.12791 | 0.494 | -0.494 | -1.455 | 3.812 |
| **g2** | 1.249 | 3.509 | 140.78 | 484.5937 | 520.983 | 929.3701 | 1574.5969 |  | -0.19446 | -0.13621 | 0.795 | -0.795 | -3.257 | 4.097 |
| **ts2** | 1.329 | 3.655 | 93.45 | 465.1742 | 566.3971 | 907.9497 | 1237.0518 | -239.7418 | -0.19025 | -0.13335 | 0.837 | -0.837 | -2.092 | 5.621 |
| **g3** | 1.359 | 4.025 | 79.73 | 453.6968 | 640.9102 | 917.7948 | 1083.5819 |  | -0.19477 | -0.13197 | 0.845 | -0.845 | -2.547 | 5.840 |
| **ts3** | 3.183 | 4.215 | 50.86 | 634.6632 | 687.7368 | 730.0102 | 954.6667 | -165.1958 | -0.20475 | -0.13264 | 1.114 | -1.114 | -4.041 | 15.342 |
| **g4** | 1.382 | 4.04 | 63.77 | 560.8301 | 636.0416 | 944.5952 | 1038.636 |  | -0.19035 | -0.12821 | 0.869 | -0.869 | -2.767 | 4.523 |
| **ts4** | 3.183 | 4.215 | 50.86 | 634.6632 | 687.7368 | 730.0102 | 954.6667 | -157.6774 | -0.20475 | -0.13264 | 1.114 | -1.114 | -4.041 | 15.342 |
| **g5** | 3.714 | 4.84 | 44.41 | 632.1592 | 704.5578 | 734.3566 | 936.9198 |  | -0.1973 | -0.13465 | 1.183 | -1.183 | -4.905 | 15.176 |
| **ts4b** | 1.59 | 4.027 | 62.77 | 556.9525 | 633.9984 | 665.4613 | 937.0388 | -120.0284 | -0.19469 | -0.14018 | 0.945 | -0.945 | -2.194 | 8.028 |
| **g5b** | 3.34 | 3.446 | 59.2 | 640.8732 | 659.7428 | 722.1593 | 939.5447 |  | -0.2076 | -0.13544 | 1.157 | -1.157 | -4.635 | 14.831 |

Table S2. Reaction path data for Mo5 + CO2.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **r(CO)** | **r(CO)** | **theta(OCO)** | **v\_bend** | **v\_bend** | **v\_symm\_stretch** | **v\_asym\_stretch** | **v\_imag** | **E(HOMO)** | **E(LUMO)** | **q(M5)** | **q(CO2)** | **E\_ads** | **E\_int** |
| **M5** |  |  |  |  |  |  |  |  | -0.17617 | -0.10727 |  |  |  |  |
| **g1** | 1.266 | 1.292 | 178.72 | 547.639 | 738.2504 | 1145.269 | 1623.5782 |  | -0.20783 | -0.10351 | 0.381 | -0.381 | -0.361 | -0.370 |
| **ts1** | 1.236 | 1.309 | 138.05 | 510.3612 | 690.1417 | 1063.9547 | 1730.6117 | -35.4775 | -0.20566 | -0.14974 | 0.374 | -0.374 | -1.320 | 0.361 |
| **g2** | 1.226 | 1.284 | 144.55 | 534.6916 | 669.9669 | 1105.3679 | 1835.1278 |  | -0.20738 | -0.13833 | 0.322 | -0.322 | -0.846 | 0.271 |
| **ts2** | 1.225 | 1.292 | 143.48 | 475.786 | 655.1531 | 1062.3144 | 1819.6708 | -76.3738 | -0.2056 | -0.15005 | 0.345 | -0.345 | -0.635 | 0.552 |
| **g3** | 1.266 | 1.291 | 137.07 | 547.5182 | 738.2949 | 1146.006 | 1623.3891 |  | -0.20784 | -0.13915 | 0.381 | -0.381 | -1.921 | -0.347 |
| **ts3** | 1.181 | 4.357 | 103.84 | 444.7586 | 475.3573 | 921.6729 | 1935.136 | -163.4808 | -0.22609 | -0.16693 | 0.395 | -0.395 | -2.033 | 5.893 |
| **g4** | 1.189 | 5.334 | 132.82 | 459.0183 | 517.1028 | 921.7447 | 1906.0104 |  | -0.22545 | -0.1685 | 0.456 | -0.456 | -2.411 | 5.469 |
| **ts4** | 1.187 | 5.975 | 153.95 | 456.1409 | 500.8111 | 919.9805 | 1906.4355 | -133.7811 | -0.22619 | -0.17042 | 0.437 | -0.437 | -2.196 | 5.563 |
| **g5** | 1.217 | 5.986 | 158.22 | 440.829 | 499.9407 | 926.185 | 1747.7452 |  | -0.22501 | -0.16152 | 0.550 | -0.550 | -2.640 | 5.341 |
| **ts5** | 1.19 | 4.223 | 169.82 | 466.5868 | 525.9877 | 811.1419 | 1904.8806 | -131.2566 | -0.22114 | -0.15059 | 0.490 | -0.491 | -2.145 | 5.871 |
| **g6** | 1.217 | 5.985 | 179.6 | 441.1896 | 500.0899 | 926.2779 | 1746.486 |  | -0.22498 | -0.1577 | 0.550 | -0.550 | -2.640 | 5.188 |
| **ts6** | 1.848 | 5.895 | 59.01 | 420.9047 | 622.0412 | 751.5739 | 936.0783 | -389.5251 | -0.23073 | -0.16672 | 0.707 | -0.707 | 0.267 | 14.653 |
| **g7** | 3.106 | 5.927 | 51.07 | 419.4157 | 734.351 | 825.2914 | 937.8582 |  | -0.23441 | -0.17585 | 0.795 | -0.795 | -0.757 | 19.878 |
| **ts7** | 3.534 | 4.825 | 64.99 | 598.9046 | 682.5529 | 714.7734 | 944.7602 | -165.1038 | -0.22265 | -0.1677 | 0.861 | -0.861 | -1.569 | 18.911 |
| **g8** | 3.196 | 4.607 | 67.67 | 641.1821 | 658.3857 | 762.3973 | 937.8894 |  | -0.22157 | -0.16408 | 0.838 | -0.838 | -2.174 | 17.503 |
| **g1b** | 1.188 | 1.191 | 179.73 | 461.5704 | 584.6698 | 1254.2387 | 2325.9287 |  | -0.17041 | -0.10319 | -0.098 | 0.098 | -0.462 | -0.466 |
| **ts1b** | 1.255 | 1.337 | 130.62 | 529.6011 | 725.6545 | 1058.9124 | 1574.3293 | -89.225 | -0.20001 | -0.14662 | 0.434 | -0.434 | -0.638 | 1.403 |
| **ts99** | 1.193 | 3.05 | 144.07 | 498.9136 | 558.4882 | 653.502 | 1898.9078 | -333.2065 | -0.20148 | -0.15754 | 0.444 | -0.444 | -1.687 | 5.683 |

Table S3. Reaction path data for Ru5 + CO2.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **r(CO)** | **r(CO)** | **theta(OCO)** | **v\_bend** | **v\_bend** | **v\_symm\_stretch** | **v\_asym\_stretch** | **v\_imag** | **E(HOMO)** | **E(LUMO)** | **q(M5)** | **q(CO2)** | **E\_ads** | **E\_int** |
| **M5** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **g1** | 1.188 | 1.19 | 179.47 | 546.1177 | 571.3651 | 1268.2408 | 2325.2175 |  | -0.18263 | -0.12757 | -0.094 | 0.094 | -0.282 | -0.452 |
| **g1ax** | 1.256 | 1.293 | 179.9 | 562.6196 | 743.4627 | 1132.0574 | 1636.6723 |  | -0.22544 | -0.11995 | 0.336 | -0.336 | -0.183 | -0.436 |
| **ts1ax** | 1.186 | 1.197 | 179.18 | 514.1069 | 574.934 | 1256.7544 | 2295.3962 | -31.5252 | -0.1895 | -0.12333 | -0.075 | 0.075 | -0.278 | -0.477 |
| **ts1eq** | 1.185 | 1.201 | 176.89 | 496.4561 | 568.8613 | 1243.5843 | 2283.9416 | -63.4888 | -0.1848 | -0.12162 | -0.076 | 0.076 | -0.048 | -0.086 |
| **g2** | 1.256 | 1.293 | 135.91 | 562.6351 | 743.5519 | 1132.3786 | 1636.5068 |  | -0.22545 | -0.1549 | 0.336 | -0.336 | -1.613 | -0.084 |
| **ts2a** | 1.183 | 4.591 | 107.71 | 446.635 | 523.6121 | 902.5708 | 1949.7494 | -32.7873 | -0.23213 | -0.17017 | 0.310 | -0.310 | -1.058 | 5.709 |
| **ts2b** | 1.183 | 5.015 | 116.12 | 444.4973 | 517.0508 | 863.1753 | 1946.4301 | -364.5112 | -0.23255 | -0.16683 | 0.321 | -0.321 | -0.262 | 7.541 |
| **g3a** | 3.733 | 5.097 | 48.66 | 527.2626 | 672.0883 | 832.3422 | 1041.2939 |  | -0.24023 | -0.1549 | 0.544 | -0.544 | -1.068 | 16.860 |
| **g3b** | 1.186 | 2.052 | 108.99 | 444.7933 | 467.5419 | 782.8741 | 1893.9572 |  | -0.22616 | -0.16425 | 0.312 | -0.312 | -1.171 | 5.572 |
| **ts3b** | 1.181 | 4.288 | 101.27 | 455.0308 | 526.3408 | 881.1852 | 1960.1749 | -207.0244 | -0.24034 | -0.16122 | 0.305 | -0.305 | -1.197 | 6.511 |
| **ts3a** | 1.184 | 6.414 | 125.93 | 458.6649 | 523.0389 | 868.9254 | 1940.2411 | -214.2944 | -0.23618 | -0.16978 | 0.331 | -0.331 | 1.923 | 9.740 |
| **g4b** | 1.225 | 4.288 | 129.9 | 450.123 | 665.8959 | 862.6002 | 1679.5299 |  | -0.23512 | -0.16392 | 0.428 | -0.428 | -1.598 | 6.260 |
| **ts4b** | 1.949 | 4.231 | 116.39 | 572.3451 | 606.7123 | 746.9317 | 869.3629 | -362.7478 | -0.23457 | -0.17434 | 0.545 | -0.545 | 1.195 | 16.343 |
| **g5b** | 2.817 | 3.344 | 144.32 | 594.969 | 638.9352 | 851.5335 | 904.8458 |  | -0.22958 | -0.16325 | 0.657 | -0.657 | -0.083 | 18.838 |

Table S4. Reaction path data for square pyramidal Rh5 + CO2.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **r(CO)** | **r(CO)** | **theta(OCO)** | **v\_bend** | **v\_bend** | **v\_symm\_stretch** | **v\_asym\_stretch** | **v\_imag** | **E(HOMO)** | **E(LUMO)** | **q(M5)** | **q(CO2)** | **E\_ads** | **E\_int** |
| **M5** |  |  |  |  |  |  |  |  | -0.19457 | -0.12282 |  |  |  |  |
| **g1** | 1.188 | 1.191 | 179.65 | 527.5153 | 571.1292 | 1266.3294 | 2328.3061 |  | -0.18479 | -0.11857 | -0.106 | 0.106 | -0.188 | -0.499 |
| **ts1** | 1.186 | 1.193 | 179.9 | 567.418 | 577.841 | 1268.8333 | 2321.1436 | -42.7174 | -0.19145 | -0.12607 | -0.111 | 0.111 | -0.303 | -0.463 |
| **g2** | 1.257 | 1.284 | 136.7 | 547.2457 | 739.7803 | 1138.4115 | 1661.5834 |  | -0.23356 | -0.15136 | 0.313 | -0.313 | -1.549 | 0.006 |
| **ts2** | 1.192 | 1.916 | 108.72 | 433.6217 | 501.5822 | 756.8841 | 1862.7199 | -570.1385 | -0.23127 | -0.1726 | 0.314 | -0.314 | -0.221 | 6.441 |
| **g3** | 1.181 | 4.164 | 108.55 | 434.2143 | 523.3141 | 862.8204 | 1961.8717 |  | -0.23573 | -0.16147 | 0.290 | -0.290 | -1.379 | 6.488 |
| **ts3** | 1.184 | 5.252 | 141.13 | 431.7459 | 516.4684 | 858.0235 | 1938.136 | -43.6664 | -0.23357 | -0.17278 | 0.306 | -0.306 | -0.751 | 7.091 |
| **g4** | 1.184 | 4.912 | 176.72 | 420.3342 | 535.0678 | 829.0629 | 1949.543 |  | -0.23842 | -0.17289 | 0.343 | -0.343 | -1.439 | 6.291 |
| **ts4** | 1.184 | 4.811 | 175.99 | 422.1787 | 535.2095 | 812.2169 | 1948.6554 | -40.2501 | -0.23745 | -0.16409 | 0.341 | -0.341 | -1.408 | 6.324 |
| **g5** | 1.184 | 3.817 | 178.87 | 534.1351 | 538.3754 | 654.2765 | 1951.1195 |  | -0.22691 | -0.15832 | 0.376 | -0.376 | -1.976 | 5.748 |
| **ts5** | 1.203 | 3.889 | 155.41 | 458.5073 | 478.8507 | 666.3458 | 1797.1666 | -182.3379 | -0.23272 | -0.17053 | 0.434 | -0.434 | -1.488 | 6.432 |
| **g6** | 1.206 | 3.206 | 130.61 | 481.4524 | 519.0718 | 592.9379 | 1776.7693 |  | -0.23312 | -0.16898 | 0.373 | -0.373 | -1.345 | 6.466 |
| **ts6** | 1.893 | 3.41 | 108.57 | 573.6224 | 606.6085 | 669.5842 | 769.6552 | -385.9373 | -0.2279 | -0.15977 | 0.568 | -0.567 | 1.099 | 15.938 |
| **g7** | 2.848 | 3.132 | 87.98 | 541.5395 | 548.8976 | 574.4191 | 940.003 |  | -0.22501 | -0.16135 | 0.571 | -0.571 | 0.094 | 19.275 |

Table S5. Reaction path data for trigonal bipyramidal Rh5 + CO2.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **r(CO)** | **r(CO)** | **theta(OCO)** | **v\_bend** | **v\_bend** | **v\_symm\_stretch** | **v\_asym\_stretch** | **v\_imag** | **E(HOMO)** | **E(LUMO)** | **q(M5)** | **q(CO2)** | **E\_ads** | **E\_int** |
| **M5** |  |  |  |  |  |  |  |  | -0.20411 | -0.16420 |  |  |  |  |
| **g1a** | 1.185 | 1.192 | 179.56 | 583.2764 | 586.5111 | 1280.8311 | 2325.8134 |  | -0.1949 | -0.15578 | -0.086 | 0.086 | -0.301 | -0.346 |
| **ts1a** | 1.188 | 1.196 | 176.68 | 502.5495 | 576.4459 | 1253.8723 | 2288.3903 | -21.2747 | -0.20632 | -0.16325 | -0.037 | 0.037 | -0.245 | -0.278 |
| **g2** | 1.244 | 1.28 | 137.77 | 551.3403 | 752.1013 | 1157.0142 | 1709.4021 |  | -0.22953 | -0.1761 | 0.286 | -0.286 | -1.340 | -0.041 |
| **ts2a** | 1.175 | 2.213 | 106.72 | 374.559 | 448.3637 | 743.4134 | 1973.4826 | -256.7614 | -0.24211 | -0.19743 | 0.312 | -0.312 | 1.079 | 8.122 |
| **g3a** | 1.168 | 3.228 | 97.85 | 331.7614 | 458.4936 | 797.7595 | 2027.9319 |  | -0.24313 | -0.19722 | 0.297 | -0.297 | 0.938 | 8.810 |
| **ts3a** | 1.202 | 3.262 | 115.17 | 426.0474 | 589.6891 | 766.72 | 1799.3546 | -61.5642 | -0.24833 | -0.20069 | 0.430 | -0.430 | 0.886 | 8.892 |
| **g4a** | 1.219 | 3.622 | 122.04 | 456.4636 | 528.0847 | 773.1791 | 1700.4791 |  | -0.24231 | -0.19023 | 0.523 | -0.523 | 0.504 | 8.479 |
| **ts4a** | 2.288 | 4.438 | 120.46 | 609.8147 | 619.1497 | 735.1472 | 789.0033 | -276.8171 | -0.25253 | -0.19443 | 0.665 | -0.665 | 4.453 | 22.307 |
| **g5a** | 3.128 | 3.672 | 83.33 | 555.0175 | 574.5098 | 587.3889 | 814.4079 |  | -0.24347 | -0.17528 | 0.808 | -0.808 | 1.993 | 22.556 |
| **g1b** | 1.185 | 1.192 | 179.76 | 581.2325 | 586.6236 | 1277.9195 | 2325.2682 |  | -0.19744 | -0.15626 | -0.088 | 0.088 | -0.368 | -0.369 |
| **ts1b** | 1.188 | 1.209 | 170.5 | 459.9236 | 566.3176 | 1220.8677 | 2231.8165 | -103.9079 | -0.20638 | -0.1649 | -0.008 | 0.008 | -0.282 | -0.208 |

Table S6. Reaction path data for Pd5 + CO2.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **r(CO)** | **r(CO)** | **theta(OCO)** | **v\_bend** | **v\_bend** | **v\_symm\_stretch** | **v\_asym\_stretch** | **v\_imag** | **E(HOMO)** | **E(LUMO)** | **q(M5)** | **q(CO2)** | **E\_ads** | **E\_int** |
| **M5** |  |  |  |  |  |  |  |  | -0.21464 | -0.16831 |  |  |  |  |
| **g1** | 1.185 | 1.192 | 178.33 | 552.1728 | 564.1784 | 1276.7019 | 2336.0679 |  | -0.20602 | -0.1623 | -0.121 | 0.121 | -0.516 | -0.547 |
| **ts1** | 1.215 | 1.294 | 145.41 | 546.2618 | 647.6853 | 1066.4911 | 1862.371 | -34.2677 | -0.23724 | -0.19405 | 0.247 | -0.247 | -0.827 | 0.242 |
| **g2** | 1.251 | 1.298 | 133.21 | 573.3993 | 767.5551 | 1152.5905 | 1634.2055 |  | -0.23291 | -0.18442 | 0.295 | -0.295 | -1.673 | -0.098 |
| **ts2** | 1.255 | 1.278 | 140.36 | 448.9557 | 623.1653 | 1079.2427 | 1675.0853 | -169.5442 | -0.24172 | -0.19034 | 0.264 | -0.263 | -0.571 | 0.771 |
| **g3** | 1.209 | 3.264 | 103.51 | 462.9402 | 630.6249 | 838.0781 | 1764.8714 |  | -0.25787 | -0.2017 | 0.420 | -0.420 | -0.769 | 7.107 |
| **ts3** | 1.189 | 3.252 | 92.49 | 435.996 | 510.321 | 835.265 | 1894.3152 | -227.5451 | -0.24824 | -0.19969 | 0.328 | -0.328 | -0.587 | 7.431 |
| **g4** | 1.176 | 4.609 | 116.23 | 404.1526 | 524.1259 | 873.8564 | 2005.8629 |  | -0.25566 | -0.20346 | 0.257 | -0.257 | -1.504 | 6.456 |
| **ts4** | 2.073 | 5.061 | 109.82 | 348.9429 | 573.7709 | 864.1135 | 918.9867 | -313.2943 | -0.26258 | -0.20524 | 0.472 | -0.472 | 3.850 | 20.434 |
| **g5** | 3.265 | 4.147 | 106.22 | 469.582 | 640.5195 | 864.4903 | 1006.0145 |  | -0.26689 | -0.20686 | 0.556 | -0.556 | 2.666 | 24.241 |

Table S7. Reaction path data for trigonal bipyramidal Pt5 + CO2.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **r(CO)** | **r(CO)** | **theta(OCO)** | **v\_bend** | **v\_bend** | **v\_symm\_stretch** | **v\_asym\_stretch** | **v\_imag** | **E(HOMO)** | **E(LUMO)** | **q(M5)** | **q(CO2)** | **E\_ads** | **E\_int** |
| **M5** |  |  |  |  |  |  |  |  | -0.20293 | -0.16110 |  |  |  |  |
| **p\_ax** | 1.186 | 1.195 | 178.480 | 550.943 | 570.3298 | 1260.5167 | 2309.7549 |  | -0.20088 | -0.15698 | -0.095 | 0.095 | -0.360 | -0.377 |
| **p\_eq** | 1.185 | 1.192 | 178.97 | 558.9764 | 576.1973 | 1275.9527 | 2330.1125 |  | -0.19635 | -0.15503 | -0.114 | 0.114 | -0.367 | -0.389 |
| **g1** | 1.186 | 1.195 | 178.48 | 550.943 | 570.3298 | 1260.5167 | 2309.7549 |  | -0.20088 | -0.15698 | -0.095 | 0.095 | -0.360 | -0.377 |
| **ts1** | 1.247 | 1.247 | 145.54 | 570.0216 | 652.2718 | 1148.0578 | 1770.136 | -147.5884 | -0.23722 | -0.18784 | 0.332 | -0.332 | -0.511 | 0.448 |
| **g2** | 1.219 | 1.302 | 143.12 | 545.792 | 669.8298 | 1060.546 | 1824.6552 |  | -0.23721 | -0.19014 | 0.306 | -0.306 | -0.843 | 0.349 |
| **ts2** | 1.217 | 1.98 | 106.89 | 468.3475 | 595.7926 | 688.3904 | 1711.4745 | -275.5387 | -0.23516 | -0.1864 | 0.393 | -0.393 | 0.247 | 7.134 |
| **g3** | 1.206 | 4.755 | 133.12 | 450.5655 | 550.314 | 851.4642 | 1791.8624 |  | -0.24728 | -0.20701 | 0.384 | -0.384 | -0.876 | 7.202 |

Table S8. Reaction path data for square pyramidal Pt5 + CO2.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **r(CO)** | **r(CO)** | **theta(OCO)** | **v\_bend** | **v\_bend** | **v\_symm\_stretch** | **v\_asym\_stretch** | **v\_imag** | **E(HOMO)** | **E(LUMO)** | **q(M5)** | **q(CO2)** | **E\_ads** | **E\_int** |
| **M5** |  |  |  |  |  |  |  |  | -0.19323 | -0.10833 |  |  |  |  |
| **g1** | 1.187 | 1.192 | 179.53 | 593.1877 | 605.0678 | 1280.5118 | 2314.224 |  | -0.18647 | -0.10337 | -0.043 | 0.043 | -0.133 | -0.133 |
| **ts1** | 1.199 | 1.217 | 160.9 | 298.097 | 474.8337 | 1152.3698 | 2120.7417 | -266.5709 | -0.19386 | -0.11235 | 0.112 | -0.112 | 0.038 | 0.298 |
| **g2** | 1.235 | 1.283 | 136.77 | 429.3525 | 681.0263 | 1146.1249 | 1696.3928 |  | -0.22775 | -0.1213 | 0.357 | -0.357 | -0.289 | 1.129 |
| **ts2** | 1.164 | 2.327 | 104.89 | 272.9111 | 304.4031 | 428.0552 | 2037.3838 | -56.497 | -0.2379 | -0.11756 | 0.244 | -0.245 | 1.767 | 9.174 |

Table S9. Reaction path data for Ag5 + CO2.

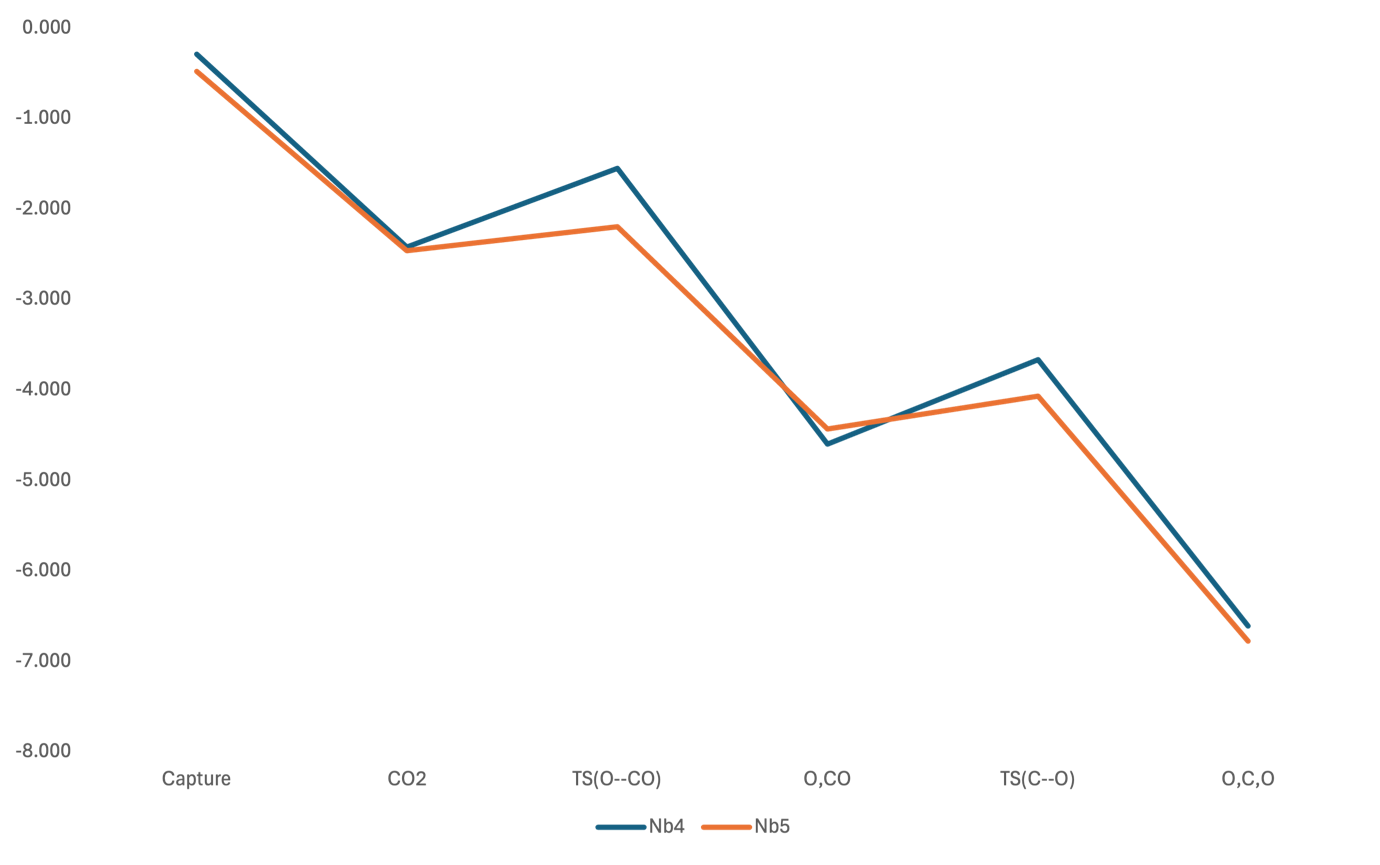


Figure S1: Reaction profile comparing key species in the addition of CO2 to Nb4 vs Nb5. Energies (E\_ads) in eV.

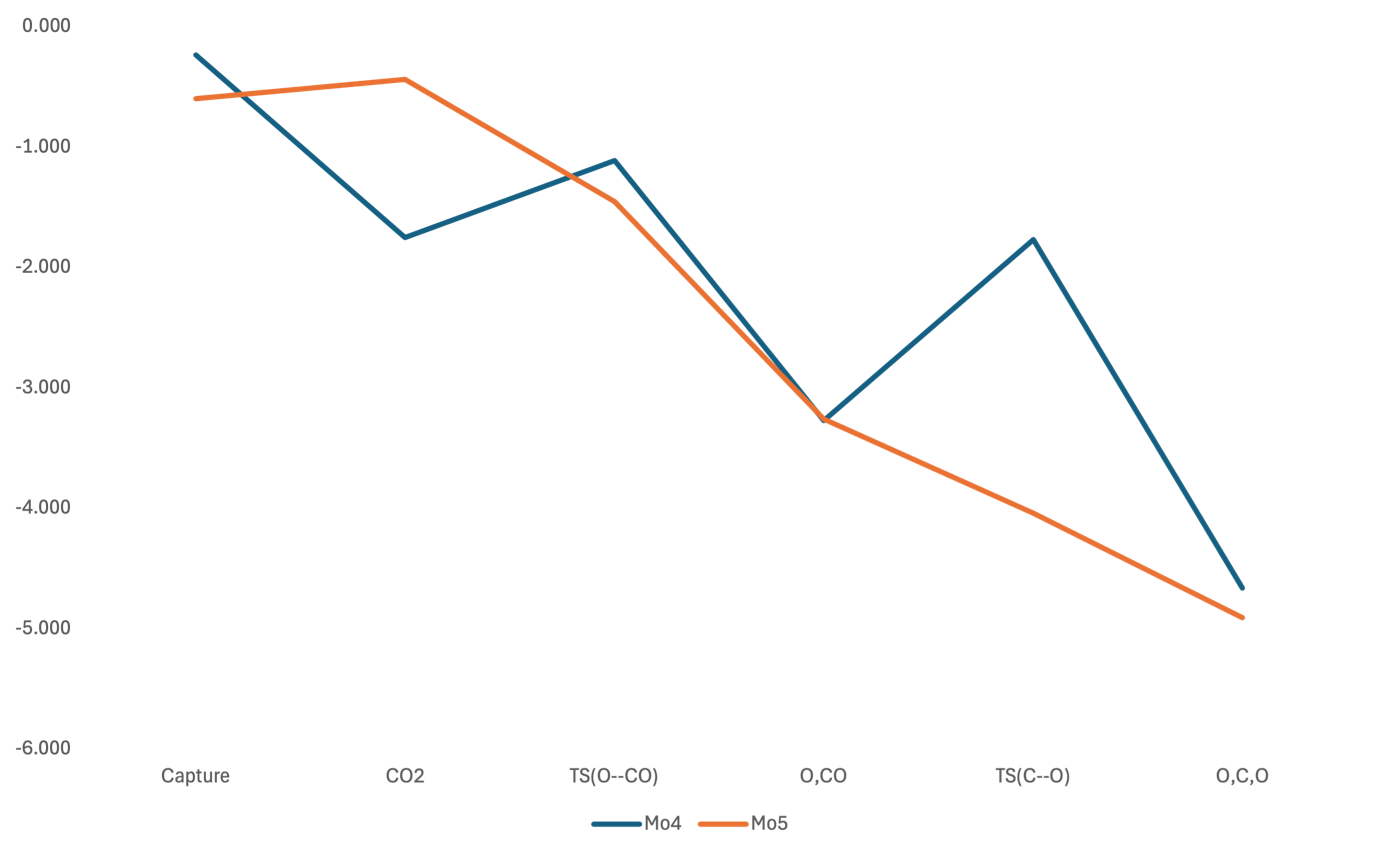


Figure S2: Reaction profile comparing key species in the addition of CO2 to Mo4 vs Mo5. Energies (E\_ads) in eV.

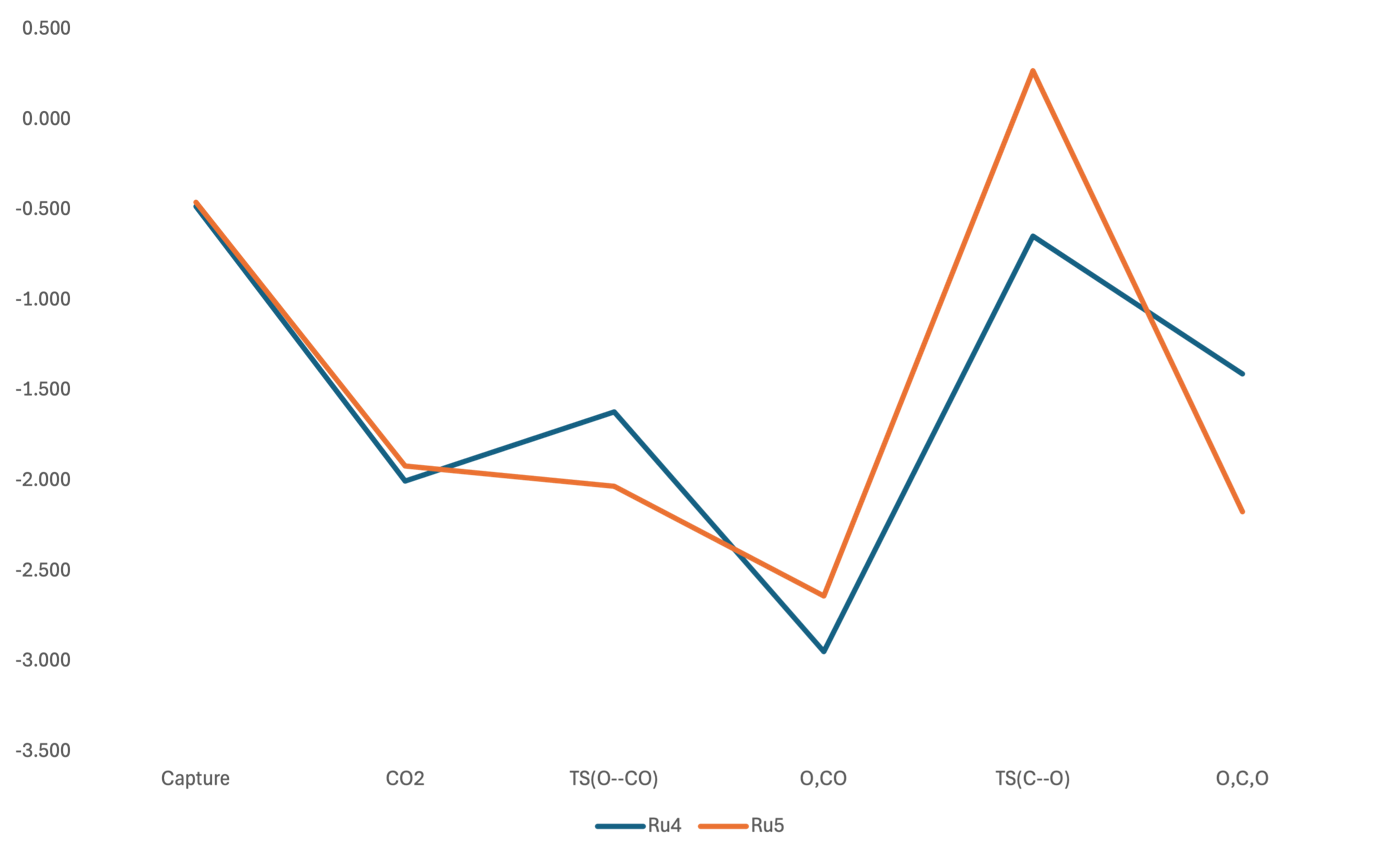


Figure S3: Reaction profile comparing key species in the addition of CO2 to Ru4 vs Ru5. Energies (E\_ads) in eV.

A line graph with orange and blue lines

AI-generated content may be incorrect.

Figure S4: Reaction profile comparing key species in the addition of CO2 to Rh4 vs Rh5. Energies (E\_ads) in eV.

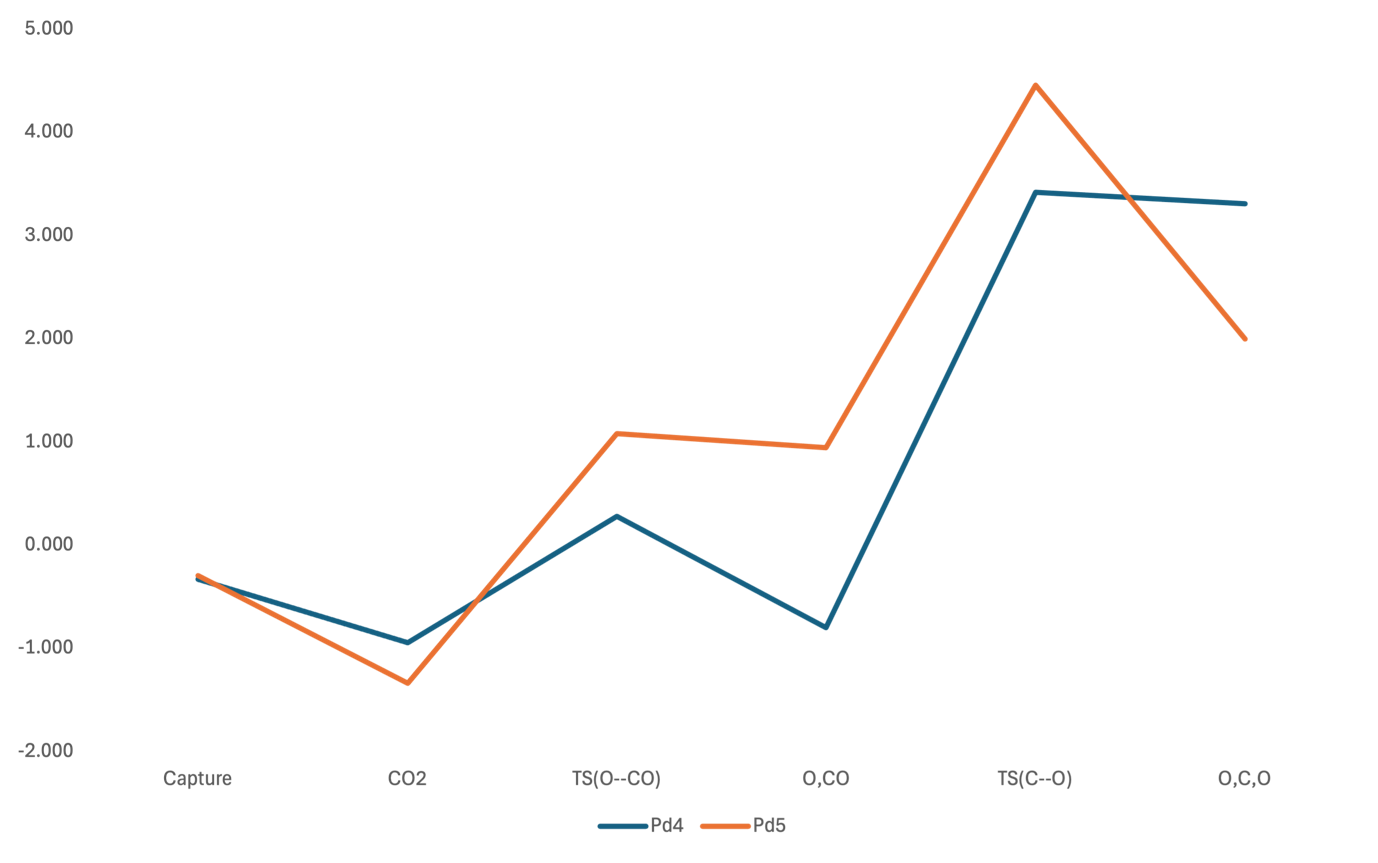


Figure S5: Reaction profile comparing key species in the addition of CO2 to Pd4 vs Pd5. Energies (E\_ads) in eV.

A graph with blue and orange lines

AI-generated content may be incorrect.

Figure S5: Reaction profile comparing key species in the addition of CO2 to Ag4 vs Ag5. Energies (E\_ads) in eV.

A graph with blue and orange lines

AI-generated content may be incorrect.

Figure S5: Reaction profile comparing key species in the addition of CO2 to Pt4 vs Pt5. Energies (E\_ads) in eV.