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


# Electronic Supplementary Information

## *Carbon Monoxide Activation by Atomic Thorium: Ground and Excited State Reaction Pathways*

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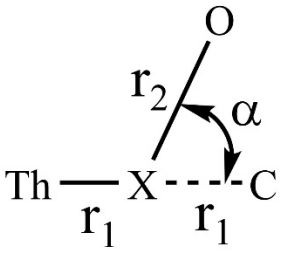


**Figure S1.** Distances $r_1$, $r_2$, and angle α used in Tables S1 and S2.

**Table S1.** CASPT2 optimized structures used for Figure 5. The distances $r_1$, $r_2$, and the angle α are defined in Figure S1.

| $1^3A''$ | | |
|---|---|---|
| α, degrees (fixed) | $r_1$, Å (optimized) | $r_2$, Å (optimized) |
| 1 | 1.14067353 | 2.31492915 |
| 10 | 1.14299506 | 2.28481856 |
| 20 | 1.14555774 | 2.19220878 |
| 30 | 1.12352955 | 2.04915771 |
| 40 | 1.11454318 | 1.84150588 |
| 50 | 1.22916889 | 1.54405012 |
| 60 | 1.17351530 | 1.39486400 |
| 70 | 1.13309395 | 1.37407871 |
| 80 | 1.13394275 | 1.42998686 |
| 90 | 1.13728374 | 1.55921696 |
| 100 | 1.13982889 | 1.77067613 |
| 105 | 1.15514007 | 1.85178563 |
| 110 | 1.16839360 | 1.94490493 |
| 115 | 1.17969135 | 2.05144268 |
| 125 | 1.19525139 | 2.28709122 |
| 132 | 1.20570972 | 2.45320525 |
| 140 | 1.22253451 | 2.63694825 |

**Table S2.** MRCI optimized structures used for Figure 6. See Figure S1 for the definition of $r_1$, $r_2$, α.

| | $^3A'$ | | $^5A''$ | | $1^3A''$ | |
|---|---|---|---|---|---|---|
| α, degrees (fixed) | $r_1$, Å (optimized) | $r_2$, Å (optimized) | $r_1$, Å (optimized) | $r_2$, Å (optimized) | $r_1$, Å (optimized) | $r_2$, Å (optimized) |
| 105 | 1.13863170 | 1.86856739 | 1.16403045 | 1.86666364 | 1.17690479 | 1.84373232 |
| 110 | 1.07371041 | 2.01922835 | 1.17702830 | 1.95938240 | 1.19164024 | 1.93751114 |
| 120 | 1.08951712 | 2.21556742 | 1.19892201 | 2.18150118 | 1.21456167 | 2.16280355 |
| 130 | 1.10144943 | 2.42532268 | 1.21670783 | 2.42163589 | 1.23351412 | 2.40841030 |
| 140 | 1.11153558 | 2.62568409 | 1.23194077 | 2.65357903 | 1.24798706 | 2.64587161 |

**Table S3.** CASSCF occupation numbers of the active orbitals for the lowest five states of OThC.

| State | 15a′ | 16a′ | 17a′ | 18a′ | 19a′ | 20a′ | 21a′ | 5a″ | 6a″ | 7a″ | 8a″ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $^3A'$ | 1.96 | 0.98 | 0.99 | 0.01 | 0.04 | 0.02 | 0.01 | 1.96 | 1.93 | 0.06 | 0.04 |
| $^5A''$ | 1.96 | 1.00 | 1.00 | 1.00 | 0.00 | 0.00 | 0.03 | 1.96 | 1.00 | 0.03 | 0.00 |
| $1^3A''$ | 1.97 | 1.23 | 0.99 | 0.76 | 0.01 | 0.03 | 0.01 | 1.96 | 0.99 | 0.04 | 0.01 |
| $2^3A''$ | 1.95 | 1.86 | 0.98 | 0.11 | 0.04 | 0.02 | 0.02 | 1.96 | 0.98 | 0.03 | 0.03 |
| $^1A'$ | 1.96 | 1.93 | 0.05 | 0.01 | 0.00 | 0.03 | 0.02 | 1.97 | 1.95 | 0.05 | 0.03 |