

Supplementary Material

Table S1. Gaussian Basis Sets Employed

| atom | type | nr | basis orbitals | contractions | ref |
|------|----------|----|--------------------|--------------------|------|
| Re | HW | I | (8s6p3d)/(3s3p2d) | (341/321/21) | (21) |
| C,O | AE | I | (10s5p1d)/(3s2p1d) | (721/41/1) | (22) |
| H | AE | I | (4s1p)/(2s1p) | (31/1) | (22) |
| Re | SP | II | (8s7p6d)/(6s5p3d) | (311111/22111/411) | (23) |
| C | 6-31G(d) | II | (10s4p1d)/(3s2p1d) | (631/31/1) | (24) |
| O | 6-31G(d) | II | (10s4p1d)/(3s2p1d) | (631/31/1) | (24) |
| H | 6-31G(d) | II | (5s)/(3s) | (31) | (24) |

Table S2. Optimized Geometries of Me₃ReO₂ Deduced From Calculations Using Different Basis Functions and Methods ^a

| parameter | GED exp | BPW91 II | BPW91 I | HF I |
|---------------------------------------|------------|-------------|------------|---------|
| Re-C _{eq} | 2.199(22) | 2.146 | 2.193 | 2.189 |
| Re-C _{ax} | 2.122(6) | 2.094 | 2.130 | 2.145 |
| Re-O1 | | 1.693 | 1.739 | 1.693 |
| Re-O2 | | 1.692 | 1.738 | 1.691 |
| Re-O _{av} | 1.703(3) | 1.693 | 1.739 | 1.692 |
| C _{eq} -H11 | | 1.109 | 1.107 | 1.086 |
| C _{eq} -H12 | | 1.101 | 1.099 | 1.077 |
| C _{ax} -H21 | | 1.109 | 1.109 | 1.084 |
| C _{ax} -H22 | | 1.101 | 1.099 | 1.077 |
| C-H _{av} | 1.115(9) | 1.104 | 1.102 | 1.080 |
| ∠CReC | 146.9(22) | 150.9 | 148.5 | 148.2 |
| ∠C _{eq} ReO1 | | 118.2 | 116.6 | 117.7 |
| ∠C _{eq} ReO2 | | 120.5 | 119.3 | 118.6 |
| ∠C _{eq} ReO _{av} | 118.5(10) | 119.4 | 118.0 | 118.2 |
| ∠OReO | | 121.3 | 124.1 | 123.7 |
| ∠ReC _{eq} H11 | | 104.4 | 103.4 | 103.8 |
| ∠ReC _{eq} H21 | | 114.0 | 113.1 | 112.5 |
| ∠ReC _{ax} H21 | | 102.8 | 100.8 | 102.1 |
| ∠ReC _{ax} H22 | | 112.7 | 112.2 | 111.0 |
| ∠ReCH _{av} | 106.5(13) | 109.9 | 108.9 | 108.6 |
| ∠H21C _{ax} ReC _{eq} | | 173.0 | 172.8 | 173.6 |

^a All bond distances in Å and angles in °.