*Supporting Information for*

# Haptotropic Shifts in Cyclopentadienyl Organometallic Complexes: Ring Folding *vs.* Ring Slippage

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## Atomic Coordinates for the optimised structures

1. $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$
2. $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$
3. $[(\eta^1\text{-}Cp)Mn(CO)_3]^{2-}$
4. $[(\eta^2\text{-}Cp)Re(CO)_3]^{2-}$
5. $[(\eta^5\text{-}Cp)_2Mn(CO)_2]^{3+}$
6. $[(\eta^5\text{-}Cp)_2Re(CO)_2]^{3+}$
7. $[(\eta^3\text{-}Cp)(\eta^5\text{-}Cp)Re(CO)_2]^{+}$ (alternated Cps)
8. $[(\eta^3\text{-}Cp)(\eta^5\text{-}Cp)Re(CO)_2]^{+}$ (eclipsed Cps)
9. $[(\eta^2\text{-}Cp)(\eta^5\text{-}Cp)Mn(CO)_2]^{+}$
10. $[(\eta^3\text{-}Cp)(\eta^5\text{-}Cp)Mn(CO)_2]^{+}$

**1. [($\eta^5$-$C_5H_5$)Mn(CO)$_3$]**

| Atomic Number | x | y | z |
|---|---|---|---|
| 25 | 3.0499 | 0.0774 | 1.2676 |
| 8 | 5.2249 | 2.0472 | 1.5507 |
| 8 | 0.9324 | 2.1091 | 0.9874 |
| 8 | 2.6393 | -0.2488 | 4.1686 |
| 6 | 4.3562 | 1.2896 | 1.4596 |
| 6 | 1.7735 | 1.3268 | 1.1188 |
| 6 | 2.8017 | -0.0924 | 3.0346 |
| 6 | 4.3769 | -1.3942 | 0.3526 |
| 6 | 3.7296 | -0.6390 | -0.6782 |
| 6 | 2.3328 | -0.8649 | -0.5669 |
| 6 | 2.1023 | -1.7437 | 0.5317 |
| 6 | 3.3750 | -2.0739 | 1.0900 |
| 1 | 5.4413 | -1.4392 | 0.5357 |
| 1 | 4.2177 | -0.0169 | -1.4150 |
| 1 | 1.5704 | -0.4281 | -1.1975 |
| 1 | 1.1427 | -2.1112 | 0.8658 |
| 1 | 3.5448 | -2.7204 | 1.9401 |

**2. [($\eta^5$-$C_5H_5$)Re(CO)$_3$]**

| Atomic Number | x | y | z |
|---|---|---|---|
| 75 | 2.2187 | 3.7084 | 4.1671 |
| 6 | 0.9064 | 2.0375 | 3.1597 |
| 6 | 1.5203 | 2.8057 | 2.1114 |
| 6 | 2.9281 | 2.6247 | 2.2082 |
| 6 | 3.2002 | 1.7496 | 3.3072 |
| 6 | 1.9421 | 1.3928 | 3.8907 |
| 6 | 0.8490 | 5.0341 | 4.3758 |
| 6 | 3.5585 | 5.0768 | 4.0710 |
| 6 | 2.4436 | 3.6094 | 6.0689 |
| 8 | -0.0202 | 5.8007 | 4.4536 |
| 8 | 4.3985 | 5.8706 | 3.9567 |
| 8 | 2.5801 | 3.4778 | 7.2148 |
| 1 | -0.1546 | 1.9488 | 3.3461 |
| 1 | 1.0034 | 3.3958 | 1.3679 |
| 1 | 3.6683 | 3.0706 | 1.5580 |
| 1 | 4.1725 | 1.3949 | 3.6171 |
| 1 | 1.8028 | 0.7383 | 4.7403 |

**3. $[(\eta^1\text{-Cp})Mn(CO)_3]^{2-}$**

| Atomic Number | x | y | z |
|---|---|---|---|
| 25 | 0.0257 | -0.1652 | -0.3626 |
| 6 | 1.3524 | 0.8350 | -1.0524 |
| 8 | 2.2160 | 1.4775 | -1.5669 |
| 6 | -1.3056 | 0.3106 | -1.4841 |
| 8 | -2.1302 | 0.6078 | -2.2889 |
| 6 | 0.4489 | -1.7614 | -1.0766 |
| 8 | 0.7291 | -2.7929 | -1.6063 |
| 6 | -0.4170 | 1.1603 | 2.4278 |
| 1 | 0.1728 | 2.0596 | 2.2723 |
| 6 | -0.0433 | -0.1526 | 1.9981 |
| 1 | 0.9732 | -0.4578 | 1.7424 |
| 6 | -1.0783 | -1.0419 | 2.4292 |
| 1 | -1.0817 | -2.1175 | 2.2745 |
| 6 | -2.0714 | -0.2865 | 3.0657 |
| 1 | -3.0132 | -0.6678 | 3.4602 |
| 6 | -1.6619 | 1.0776 | 3.0648 |
| 1 | -2.2379 | 1.9151 | 3.4583 |

**4. $[(\eta^2\text{-Cp})Re(CO)_3]^{2-}$**

| Atomic Number | x | y | z |
|---|---|---|---|
| 75 | -0.3912 | -0.0684 | -0.4407 |
| 6 | 1.4600 | -0.3192 | -0.7973 |
| 8 | 2.5878 | -0.2740 | -1.2072 |
| 6 | -1.3264 | 1.4125 | -1.1626 |
| 8 | -1.6999 | 2.4066 | -1.7309 |
| 6 | -0.8802 | -1.1062 | -1.9210 |
| 8 | -1.2339 | -1.8289 | -2.8080 |
| 6 | -0.9995 | -0.1576 | 1.9624 |
| 1 | -2.0544 | -0.1917 | 1.7079 |
| 6 | -0.1968 | 1.0325 | 1.9865 |
| 1 | -0.5252 | 2.0170 | 1.6720 |
| 6 | 0.9787 | 0.7392 | 2.7228 |
| 6 | 0.9193 | -0.6012 | 3.1455 |
| 6 | -0.2855 | -1.1613 | 2.6730 |
| 1 | -0.6217 | -2.1843 | 2.8228 |
| 1 | 1.8050 | 1.4260 | 2.8924 |
| 1 | 1.7137 | -1.1411 | 3.6581 |

**5. $[(\eta^5\text{-Cp})_2Mn(CO)_2]^{3+}$**

| Atomic Number | x | y | z |
|---|---|---|---|
| 25 | -0.0012 | 0.0003 | 0.1582 |
| 6 | -0.0343 | 1.2976 | 1.5737 |
| 8 | -0.0622 | 2.0479 | 2.4170 |
| 6 | 0.0389 | -1.2943 | 1.5760 |
| 8 | 0.0709 | -2.0429 | 2.4206 |
| 6 | -2.1906 | 0.1043 | 0.5130 |
| 6 | -1.8504 | 1.1477 | -0.4174 |
| 6 | -1.3929 | 0.5278 | -1.6080 |
| 6 | -1.4149 | -0.9123 | -1.4109 |
| 6 | -1.9273 | -1.1668 | -0.1167 |
| 1 | -2.6437 | 0.2427 | 1.4935 |
| 1 | -1.9875 | 2.2155 | -0.2627 |
| 1 | -1.1559 | 1.0363 | -2.5383 |
| 1 | -1.1977 | -1.6670 | -2.1615 |
| 1 | -2.1468 | -2.1466 | 0.3022 |
| 6 | 2.1900 | -0.1049 | 0.5021 |
| 6 | 1.9244 | 1.1661 | -0.1269 |
| 6 | 1.4050 | 0.9113 | -1.4183 |
| 6 | 1.3813 | -0.5289 | -1.6146 |
| 6 | 1.8442 | -1.1485 | -0.4260 |
| 1 | 2.6480 | -0.2430 | 1.4804 |
| 1 | 2.1467 | 2.1459 | 0.2903 |
| 1 | 1.1842 | 1.6658 | -2.1681 |
| 1 | 1.1395 | -1.0376 | -2.5436 |
| 1 | 1.9812 | -2.2164 | -0.2714 |

**6. $[(\eta^5\text{-Cp})_2Re(CO)_2]^{3+}$**

| Atomic Number | x | y | z |
|---|---|---|---|
| 75 | -0.0012 | 0.0000 | 0.1147 |
| 6 | 0.0023 | 1.3900 | 1.5872 |
| 8 | 0.0043 | 2.1696 | 2.4061 |
| 6 | 0.0020 | -1.3902 | 1.5870 |
| 8 | 0.0039 | -2.1700 | 2.4058 |
| 6 | -2.2665 | 0.0001 | 0.4890 |
| 6 | -2.0051 | 1.1710 | -0.3219 |
| 6 | -1.5391 | 0.7253 | -1.5885 |
| 6 | -1.5392 | -0.7248 | -1.5886 |
| 6 | -2.0053 | -1.1707 | -0.3221 |
| 1 | -2.7249 | 0.0001 | 1.4758 |
| 1 | -2.1842 | 2.2047 | -0.0350 |
| 1 | -1.3050 | 1.3628 | -2.4366 |
| 1 | -1.3052 | -1.3622 | -2.4369 |
| 1 | -2.1846 | -2.2044 | -0.0354 |
| 6 | 2.2657 | -0.0003 | 0.4784 |
| 6 | 2.0007 | 1.1706 | -0.3313 |
| 6 | 1.5289 | 0.7251 | -1.5957 |
| 6 | 1.5287 | -0.7250 | -1.5959 |
| 6 | 2.0004 | -1.1710 | -0.3315 |
| 1 | 2.7287 | -0.0005 | 1.4631 |
| 1 | 2.1813 | 2.2043 | -0.0451 |
| 1 | 1.2909 | 1.3627 | -2.4427 |
| 1 | 1.2906 | -1.3623 | -2.4431 |
| 1 | 2.1808 | -2.2048 | -0.0457 |

**7. $[(\eta^3\text{-Cp})(\eta^5\text{-Cp})Re(CO)_2]^+$ (alternated Cps)**

| Atomic Number | x | y | z |
|---|---|---|---|
| 75 | -0.2342 | 0.0000 | -0.0461 |
| 6 | 0.2723 | 1.2864 | 1.3002 |
| 8 | 0.4923 | 2.0658 | 2.1194 |
| 6 | 0.2723 | -1.2860 | 1.3004 |
| 8 | 0.4924 | -2.0653 | 2.1198 |
| 6 | -2.4685 | -0.0001 | 0.4141 |
| 6 | -2.2161 | 1.1576 | -0.3954 |
| 6 | -1.8098 | 0.7135 | -1.6877 |
| 6 | -1.8096 | -0.7137 | -1.6877 |
| 6 | -2.2159 | -1.1578 | -0.3954 |
| 1 | -2.8486 | -0.0002 | 1.4267 |
| 1 | -2.3457 | 2.1873 | -0.0895 |
| 1 | -1.5530 | 1.3509 | -2.5240 |
| 1 | -1.5527 | -1.3512 | -2.5240 |
| 1 | -2.3453 | -2.1876 | -0.0894 |
| 6 | 1.3893 | 0.0002 | -1.5401 |
| 6 | 1.8544 | -1.1366 | -0.8110 |
| 6 | 2.9105 | -0.6761 | 0.1224 |
| 6 | 2.9107 | 0.6760 | 0.1224 |
| 6 | 1.8548 | 1.1368 | -0.8110 |
| 1 | 0.9663 | 0.0002 | -2.5358 |
| 1 | 1.7135 | -2.1643 | -1.1242 |
| 1 | 3.5221 | -1.3370 | 0.7224 |
| 1 | 3.5225 | 1.3367 | 0.7224 |
| 1 | 1.7140 | 2.1645 | -1.1241 |

**8. $[(\eta^3\text{-Cp})(\eta^5\text{-Cp})Re(CO)_2]^+$ (eclipsed Cps)**

| Atomic Number | x | y | z |
|---|---|---|---|
| 75 | -0.0736 | 0.0003 | 0.4173 |
| 6 | 0.0364 | 1.2882 | 1.8668 |
| 8 | 0.0597 | 2.0640 | 2.7139 |
| 6 | 0.0382 | -1.2853 | 1.8687 |
| 8 | 0.0624 | -2.0598 | 2.7170 |
| 6 | -2.3684 | -0.0013 | 0.3296 |
| 6 | -1.9088 | 1.1494 | -0.3833 |
| 6 | -1.2418 | 0.7035 | -1.5756 |
| 6 | -1.2408 | -0.7077 | -1.5745 |
| 6 | -1.9072 | -1.1526 | -0.3815 |
| 1 | -2.9519 | -0.0010 | 1.2400 |
| 1 | -2.1020 | 2.1803 | -0.1175 |
| 1 | -0.8161 | 1.3440 | -2.3345 |
| 1 | -0.8143 | -1.3489 | -2.3323 |
| 1 | -2.0990 | -2.1834 | -0.1140 |
| 6 | 2.1765 | 0.0029 | 0.4129 |
| 6 | 1.9134 | 1.1360 | -0.4141 |
| 6 | 1.9097 | 0.6785 | -1.8171 |
| 6 | 1.9105 | -0.6794 | -1.8152 |
| 6 | 1.9147 | -1.1330 | -0.4107 |
| 1 | 2.6004 | 0.0046 | 1.4072 |
| 1 | 2.0484 | 2.1660 | -0.1064 |
| 1 | 1.8565 | 1.3374 | -2.6741 |
| 1 | 1.8582 | -1.3409 | -2.6703 |
| 1 | 2.0518 | -2.1619 | -0.1003 |

**9. $[(\eta^2\text{-Cp})(\eta^5\text{-Cp})Mn(CO)_2]^+$**

| Atomic Number | x | y | z |
|---|---|---|---|
| 25 | -0.1680 | 0.1340 | 0.5090 |
| 6 | -0.1336 | 1.6383 | 1.5563 |
| 8 | -0.1310 | 2.5909 | 2.1899 |
| 6 | -0.0536 | -0.8279 | 2.0657 |
| 8 | -0.0007 | -1.4502 | 3.0242 |
| 6 | -2.3221 | 0.0540 | 0.4416 |
| 6 | -1.8771 | 1.0490 | -0.4763 |
| 6 | -1.1343 | 0.4017 | -1.5130 |
| 6 | -1.0925 | -0.9789 | -1.2237 |
| 6 | -1.8087 | -1.1976 | -0.0051 |
| 1 | -2.9243 | 0.2207 | 1.3244 |
| 1 | -2.1054 | 2.1057 | -0.4281 |
| 1 | -0.7086 | 0.8898 | -2.3770 |
| 1 | -0.6280 | -1.7471 | -1.8239 |
| 1 | -1.9770 | -2.1575 | 0.4655 |
| 6 | 1.8845 | -0.5729 | 0.3025 |
| 6 | 1.8411 | 0.8227 | 0.0195 |
| 6 | 1.8940 | 0.9536 | -1.4254 |
| 6 | 2.0117 | -0.3112 | -2.0128 |
| 6 | 1.9657 | -1.2522 | -0.9789 |
| 1 | 2.2814 | -1.0118 | 1.2095 |
| 1 | 2.2004 | 1.6028 | 0.6793 |
| 1 | 1.8584 | 1.8991 | -1.9564 |
| 1 | 2.0450 | -0.5248 | -3.0731 |
| 1 | 1.9954 | -2.3300 | -1.0995 |

**10. $[(\eta^3\text{-Cp})(\eta^5\text{-Cp})Mn(CO)_2]^+$**

| Atomic Number | x | y | z |
|---|---|---|---|
| 25 | -0.2268 | 0.0000 | -0.0496 |
| 6 | 0.2104 | 1.2600 | 1.2062 |
| 8 | 0.3719 | 2.0470 | 2.0232 |
| 6 | 0.2112 | -1.2585 | 1.2072 |
| 8 | 0.3733 | -2.0448 | 2.0247 |
| 6 | -2.3140 | -0.0006 | 0.5125 |
| 6 | -2.0729 | 1.1529 | -0.2964 |
| 6 | -1.6698 | 0.7104 | -1.5835 |
| 6 | -1.6691 | -0.7126 | -1.5830 |
| 6 | -2.0718 | -1.1545 | -0.2955 |
| 1 | -2.6532 | -0.0004 | 1.5397 |
| 1 | -2.1885 | 2.1827 | 0.0148 |
| 1 | -1.4058 | 1.3489 | -2.4162 |
| 1 | -1.4044 | -1.3514 | -2.4152 |
| 1 | -2.1864 | -2.1842 | 0.0164 |
| 6 | 1.3067 | 0.0011 | -1.5009 |
| 6 | 1.7648 | -1.1344 | -0.7857 |
| 6 | 2.7712 | -0.6776 | 0.1976 |
| 6 | 2.7719 | 0.6778 | 0.1979 |
| 6 | 1.7661 | 1.1358 | -0.7852 |
| 1 | 0.8405 | 0.0017 | -2.4740 |
| 1 | 1.6214 | -2.1632 | -1.0940 |
| 1 | 3.3585 | -1.3366 | 0.8236 |
| 1 | 3.3598 | 1.3359 | 0.8243 |
| 1 | 1.6230 | 2.1649 | -1.0925 |