Dimetallocene Carbonyls of the Third Row Transition Metals: The Quest for High Order Metal-Metal Multiple Bonds

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Supporting Information

Tables S1-S10: Theoretical harmonic vibrational frequencies for $Cp_2M_2(CO)$ (M = Os, Re, W, Ta) using the BP86 method.

Tables S11-S43: Theoretical Cartesian coordinates $Cp_2M_2(CO)$ (M = Os, Re, W, Ta) using the MPW1PW91 method..

Complete Gaussian 03 reference (Reference 48)

Table S1. Theoretical harmonic vibrational frequencies (in cm^{-1}) for structures of $Cp_2Os_2(CO)$ using the BP86/SDD method (infrared intensities in parentheses are in km/mol).

OsI-S	OsI-T	OsI-Q	OsI'-Q
34.8 (b, 1.1)	23.6 (b, 2.0)	30.6 (a, 0.7)	13.3 (a", 0.0)
50.8 (a, 0.0)	30.0 (a, 0.0)	33.2 (a, 0.1)	40.6 (a", 0.3)
66.0 (b, 0.4)	51.5 (b, 0.1)	50.3 (a, 0.3)	40.7 (a', 1.6)
73.5 (a, 1.9)	60.5 (a, 1.2)	59.7 (a, 0.5)	43.8 (a', 1.2)
84.3 (b, 0.6)	87.3 (b, 2.7)	64.6 (a, 1.0)	81.6 (a', 0.3)
141.6 (a, 0.0)	105.9 (a, 0.1)	86.4 (a, 0.7)	93.2 (a", 0.5)
149.2 (b, 1.4)	124.5 (b, 3.4)	170.7 (a, 2.6)	185.1 (a', 0.4)
214.0 (a, 0.2)	204.6 (b, 1.4)	201.2 (a, 0.8)	194.7 (a", 0.9)
220.7 (b, 1.4)	206.3 (a, 0.1)	209.0 (a, 0.9)	224.8 (a", 0.5)
279.1 (a, 0.0)	270.4 (a, 0.6)	232.3 (a, 0.2)	239.8 (a", 0.5)
314.9 (b, 6.1)	290.1 (a, 2.2)	252.9 (a, 2.6)	240.0 (a', 1.3)
333.4 (b, 4.6)	291.6 (b, 2.4)	266.5 (a, 0.9)	253.6 (a', 1.4)
340.5 (a, 4.1)	310.4 (b, 0.7)	277.7 (a, 1.6)	316.1 (a", 0.3)
372.4 (a, 3.6)	331.3 (a, 6.9)	309.5 (a, 0.7)	334.7 (a', 1.3)
418.5 (b, 5.8)	364.8 (b, 0.2)	441.2 (a, 4.0)	454.4 (a', 3.0)
479.9 (a, 2.1)	462.9 (b, 9.1)	458.6 (a, 17.4)	493.7 (a', 4.2)
506.2 (b, 24.0)	477.8 (a, 1.9)	492.4 (a, 0.5)	496.3 (a", 25.2)
530.6 (b, 17.3)	528.2 (a, 0.1)	511.6 (a, 0.4)	521.3 (a', 0.4)
532.0 (a, 1.5)	531.0 (b, 3.0)	529.2 (a, 0.8)	526.7 (a", 2.9)
560.0 (a, 1.7)	545.3 (a, 0.9)	534.3 (a, 0.8)	537.0 (a', 1.0)
560.3 (b, 1.9)	546.4 (b, 1.0)	540.9 (a, 0.2)	540.8 (a", 17.7)
748.6 (b, 64.0)	756.8 (b, 90.6)	744.3 (a, 4.2)	744.1 (a", 26.7)
752.3 (a, 0.4)	759.4 (a, 0.2)	747.7 (a, 2.8)	746.8 (a', 17.0)
762.5 (b, 44.4)	775.4 (a, 0.1)	754.7 (a, 77.2)	759.3 (a', 21.0)
772.3 (a, 0.2)	776.0 (b, 24.9)	762.2 (a, 45.9)	760.9 (a", 41.3)
790.6 (a, 0.0)	780.4 (b, 12.2)	776.1 (a, 2.1)	776.6 (a', 0.4)
794.2 (b, 8.3)	780.9 (a, 1.5)	786.4 (a, 7.6)	782.0 (a", 0.1)
799.4 (b, 3.4)	796.4 (b, 3.9)	796.5 (a, 1.9)	791.8 (a", 0.1)
803.1 (a, 0.3)	801.5 (a, 0.1)	799.9 (a, 3.5)	795.6 (a', 0.2)
805.3 (b, 1.2)	806.7 (a, 0.0)	800.7 (a, 0.1)	799.9 (a", 0.6)
808.6 (a, 0.4)	808.9 (b, 0.3)	805.7 (a, 1.1)	801.2 (a', 8.2)
832.9 (b, 2.7)	829.5 (b, 2.0)	827.6 (a, 2.8)	831.2 (a", 0.8)
834.5 (a, 0.5)	829.6 (a, 0.2)	831.8 (a, 0.1)	837.0 (a", 8.0)
845.0 (b, 0.1)	843.4 (a, 1.6)	837.3 (a, 1.2)	838.1 (a', 0.1)
845.4 (a, 4.0)	845.1 (b, 4.3)	845.7 (a, 1.3)	840.7 (a', 3.9)
966.6 (b, 19.4)	975.9 (a, 16.8)	969.1 (a, 13.0)	965.4 (a", 2.5)
968.4 (a, 8.9)	976.6 (b, 11.6)	977.1 (a, 11.1)	966.5 (a', 18.4)
977.3 (b, 7.8)	983.3 (b, 16.0)	984.4 (a, 12.8)	976.5 (a", 0.0)
979.1 (a, 14.8)	984.1 (a, 10.4)	987.8 (a, 12.1)	977.5 (a', 20.7)

1024.9 (b, 0.0)	1031.2 (a, 0.1)	1031.3 (a, 1.0)	1025.7 (a", 0.5)
1028.7 (a, 0.1)	1033.5 (b, 0.2)	1034.5 (a, 0.6)	1028.9 (a', 1.2)
1036.7 (b, 1.6)	1038.7 (b, 0.1)	1036.3 (a, 1.0)	1034.4 (a", 0.0)
1039.1 (a, 1.2)	1039.3 (a, 0.6)	1037.8 (a, 0.7)	1034.8 (a', 1.3)
1083.9 (b, 20.5)	1090.6 (b, 14.8)	1088.6 (a, 9.1)	1080.5 (a", 15.1)
1084.4 (a, 0.2)	1090.9 (a, 0.4)	1092.0 (a, 4.7)	1080.7 (a', 2.6)
1214.6 (a, 0.0)	1219.0 (b, 0.0)	1218.8 (a, 0.0)	1214.6 (a", 0.0)
1214.7 (b, 0.1)	1219.0 (a, 0.0)	1220.6 (a, 0.0)	1215.0 (a', 0.0)
1325.0 (b, 0.1)	1336.7 (a, 0.0)	1333.3 (a, 0.2)	1316.3 (a", 6.9)
1328.8 (a, 0.2)	1337.0 (b, 0.4)	1335.1 (a, 0.3)	1321.5 (a', 0.3)
1340.7 (b, 0.5)	1343.7 (a, 0.3)	1343.5 (a, 7.1)	1337.3 (a", 1.1)
1343.0 (a, 1.0)	1348.5 (b, 1.1)	1348.6 (a, 0.0)	1339.9 (a', 3.9)
1377.3 (b, 3.7)	1391.9 (a, 0.6)	1379.9 (a, 4.1)	1383.8 (a', 2.6)
1378.5 (a, 1.1)	1392.5 (b, 4.6)	1389.2 (a, 4.0)	1384.1 (a", 6.5)
1411.6 (b, 1.0)	1400.2 (a, 2.4)	1403.7 (a, 3.3)	1387.5 (a", 0.9)
1413.8 (a, 0.9)	1402.1 (b, 2.3)	1410.5 (a, 0.5)	1389.5 (a', 4.4)
1802.4 (a, 603.5)	1808.5 (a, 634.1)	1755.9 (a, 629.3)	1724.9 (a', 538.5)
3165.6 (b, 0.5)	3170.7 (a, 0.0)	3168.8 (a, 0.0)	3167.2 (a", 0.4)
3166.0 (a, 0.1)	3170.8 (b, 0.0)	3170.6 (a, 0.0)	3167.3 (a', 0.4)
3175.2 (a, 0.0)	3173.7 (b, 0.0)	3173.7 (a, 0.1)	3173.2 (a", 0.2)
3175.3 (b, 0.1)	3174.0 (a, 0.0)	3177.0 (a, 0.3)	3173.2 (a', 0.4)
3183.0 (b, 1.2)	3184.0 (a, 0.2)	3182.6 (a, 0.5)	3180.9 (a", 0.0)
3183.3 (a, 0.1)	3184.0 (b, 0.2)	3185.8 (a, 0.1)	3181.1 (a', 1.4)
3187.2 (b, 0.1)	3186.8 (b, 0.3)	3186.3 (a, 0.4)	3187.9 (a", 0.0)
3187.3 (a, 0.2)	3187.0 (a, 0.0)	3189.2 (a, 0.1)	3188.1 (a', 0.4)
3196.0 (b, 0.5)	3196.6 (b, 0.2)	3196.2 (a, 0.3)	3196.0 (a", 0.4)
3196.1 (a, 0.0)	3196.6 (a, 0.0)	3202.7 (a, 0.5)	3196.1 (a', 1.1)

Table S2. Theoretical harmonic vibrational frequencies (in cm^{-1}) for septet structures of $Cp_2Os_2(CO)$ using the BP86/SDD method (infrared intensities in parentheses are in km/mol).

OsI-H	OsI'-H
37.4 (b, 1.0)	28.9 (a", 0.0)
40.8 (a, 0.0)	47.0 (a', 0.3)
53.6 (b, 0.2)	65.2 (a', 1.0)
54.3 (a, 0.7)	70.4 (a", 0.1)
73.7 (b, 0.0)	78.6 (a', 0.0)
83.8 (a, 0.1)	87.7 (a", 0.3)
183.0 (b, 4.8)	161.1 (a", 3.4)
191.8 (a, 0.1)	180.8 (a', 0.2)
193.7 (b, 2.7)	196.5 (a', 1.0)
204.8 (a, 0.0)	204.2 (a", 0.8)
208.8 (b, 3.3)	222.1 (a", 2.6)
224.6 (a, 0.7)	229.0 (a', 2.0)
271.5 (b, 1.5)	261.1 (a", 0.0)
275.0 (a, 0.6)	267.4 (a', 1.6)
398.4 (b, 18.5)	427.3 (a", 40.0)
455.7 (a, 0.2)	446.6 (a', 1.3)
489.2 (b, 9.2)	504.5 (a', 5.8)
513.9 (a, 1.4)	513.2 (a", 4.0)
515.5 (b, 1.8)	519.4 (a', 0.2)
550.0 (b, 2.7)	551.5 (a", 0.2)
552.0 (a, 0.5)	554.7 (a', 0.8)
745.2 (b, 133.1)	727.6 (a", 40.0)
747.4 (a, 6.9)	745.5 (a', 88.5)
754.7 (b, 20.4)	749.8 (a", 0.3)
758.3 (b, 13.3)	754.9 (a', 3.7)
758.5 (a, 15.3)	763.7 (a", 29.2)
764.1 (a, 0.0)	765.0 (a', 21.6)
797.7 (b, 0.3)	797.9 (a", 0.2)
801.7 (b, 0.2)	801.4 (a', 0.2)
801.9 (a, 0.9)	802.4 (a", 0.0)
802.1 (a, 0.0)	805.2 (a', 0.5)
826.3 (b, 3.5)	823.6 (a", 1.0)
826.3 (a, 3.7)	830.8 (a", 0.1)
838.4 (a, 2.5)	831.2 (a', 3.1)
839.6 (b, 1.7)	836.4 (a', 5.7)
980.8 (b, 27.9)	978.9 (a", 10.9)
982.2 (a, 3.3)	980.5 (a', 12.6)
985.0 (b, 6.5)	985.0 (a", 3.3)
985.2 (a, 20.3)	986.4 (a', 25.9)

1033.3 (a, 0.0)	1032.1 (a", 1.1)
1034.2 (b, 0.9)	1034.3 (a', 0.0)
1040.7 (b, 0.2)	1034.9 (a", 0.3)
1042.5 (a, 0.1)	1041.6 (a', 1.1)
1092.7 (a, 0.5)	1092.5 (a", 1.7)
1092.7 (b, 2.3)	1093.7 (a', 2.6)
1220.7 (b, 0.0)	1219.5 (a", 0.0)
1221.0 (a, 0.0)	1220.8 (a', 0.0)
1334.1 (a, 0.3)	1332.5 (a", 2.4)
1335.8 (b, 1.0)	1334.5 (a', 0.0)
1343.1 (b, 0.6)	1345.9 (a', 0.0)
1344.5 (a, 0.0)	1347.7 (a", 0.8)
1396.1 (b, 5.4)	1394.6 (a", 0.4)
1397.0 (a, 2.1)	1396.6 (a', 4.7)
1401.1 (a, 2.2)	1400.3 (a", 0.9)
1401.3 (b, 2.2)	1401.4 (a', 3.8)
1745.9 (a, 552.3)	1740.7 (a', 588.8)
3164.9 (b, 0.1)	3164.7 (a", 0.0)
3165.1 (a, 0.0)	3164.8 (a', 0.0)
3171.4 (a, 0.0)	3170.7 (a", 0.0)
3171.4 (b, 0.0)	3172.1 (a', 0.3)
3180.7 (a, 0.2)	3180.3 (a", 0.8)
3180.7 (b, 0.4)	3181.1 (a', 0.3)
3183.6 (b, 0.1)	3184.3 (a", 0.1)
3183.7 (a, 0.3)	3185.1 (a', 0.5)
3195.0 (b, 0.8)	3194.5 (a", 0.0)
3195.1 (a, 0.2)	3196.1 (a', 3.0)

Table S3. Theoretical harmonic vibrational frequencies (in cm^{-1}) for singlet and triplet structures of $Cp_2Re_2(CO)$ using the BP86/SDD method (infrared intensities in parentheses are in km/mol).

ReI-S (C_2)	**ReI-S** (C_1) MPW1PW91/SDD	**ReI-T** (C_1)
28.6 (b, 1.1)	33.3 (a, 1.2)	23.7 (a, 0.2)
39.8 (a, 0.0)	47.1 (a, 0.1)	38.5 (a, 0.8)
56.9 (a, 0.6)	60.7 (a, 0.6)	43.9 (a, 0.2)
63.8 (b, 0.6)	67.0 (a, 0.6)	58.8 (a, 0.6)
102.0 (b, 0.1)	103.3 (a, 0.1)	80.4 (a, 1.1)
132.3 (a, 0.0)	133.1 (a, 0.0)	116.6 (a, 0.1)
168.2 (b, 2.0)	169.7 (a, 2.0)	170.5 (a, 2.5)
198.2 (a, 0.3)	199.4 (a, 0.2)	202.4 (a, 0.3)
226.5 (b, 1.0)	228.5 (a, 0.9)	232.5 (a, 0.8)
270.0 (a, 0.2)	269.6 (a, 0.2)	274.5 (a, 1.1)
274.5 (b, 2.8)	274.8 (a, 2.7)	281.5 (a, 11.6)
288.5 (a, 7.6)	289.8 (a, 7.4)	305.4 (a, 1.4)
316.4 (b, 1.0)	321.3 (a, 1.2)	321.3 (a, 6.2)
334.6 (a, 3.3)	337.6 (a, 3.4)	337.5 (a, 6.1)
394.1 (b, 2.2)	394.2 (a, 2.3)	428.7 (a, 12.0)
479.7 (a, 0.7)	480.0 (a, 0.7)	469.1 (a, 8.5)
487.9 (b, 9.4)	487.6 (a, 8.9)	483.6 (a, 1.3)
540.4 (b, 8.9)	541.8 (a, 9.7)	531.3 (a, 1.0)
542.1 (a, 0.5)	543.7 (a, 0.5)	538.7 (a, 1.4)
553.5 (a, 0.6)	554.9 (a, 0.5)	546.9 (a, 2.4)
556.2 (b, 1.9)	557.8 (a, 1.5)	551.0 (a, 0.5)
748.5 (b, 88.2)	750.4 (a, 91.2)	751.5 (a, 42.2)
750.1 (a, 1.6)	752.0 (a, 1.3)	761.0 (a, 1.8)
764.5 (a, 0.1)	765.6 (a, 0.3)	763.8 (a, 2.6)
765.8 (b, 18.8)	766.8 (a, 15.9)	764.8 (a, 49.9)
789.1 (b, 28.5)	788.3 (a, 28.2)	766.5 (a, 4.8)
793.1 (a, 0.2)	793.3 (a, 0.1)	780.0 (a, 1.4)
797.6 (b, 0.9)	797.5 (a, 0.9)	794.3 (a, 4.7)
801.0 (a, 0.0)	800.9 (a, 0.1)	796.2 (a, 3.4)
806.8 (a, 0.7)	807.2 (a, 0.8)	800.7 (a, 0.2)
810.2 (b, 0.3)	810.6 (a, 0.2)	807.6 (a, 2.4)
834.3 (a, 0.3)	836.3 (a, 0.4)	824.7 (a, 3.6)
834.8 (b, 0.3)	836.4 (a, 0.3)	828.0 (a, 1.6)
847.8 (a, 1.3)	846.6 (a, 1.4)	834.5 (a, 0.5)
848.3 (b, 1.3)	847.2 (a, 1.5)	847.6 (a, 2.4)
977.2 (a, 14.9)	978.0 (a, 18.8)	972.8 (a, 17.7)
977.4 (b, 18.8)	978.5 (a, 14.6)	975.0 (a, 16.6)
983.9 (b, 9.4)	984.1 (a, 13.3)	977.4 (a, 19.9)

984.5 (a, 14.6)	984.7 (a, 10.7)	979.4 (a, 5.5)
1034.2 (a, 0.1)	1034.3 (a, 0.1)	1029.3 (a, 0.3)
1034.8 (b, 0.3)	1034.9 (a, 0.2)	1031.8 (a, 0.5)
1038.6 (b, 0.0)	1038.8 (a, 0.0)	1037.3 (a, 0.1)
1039.7 (a, 2.1)	1039.8 (a, 1.9)	1038.7 (a, 0.4)
1089.4 (a, 1.7)	1089.6 (a, 1.7)	1082.4 (a, 18.8)
1089.5 (b, 15.4)	1089.7 (a, 15.8)	1083.7 (a, 12.5)
1219.3 (b, 0.0)	1220.2 (a, 0.0)	1216.7 (a, 0.0)
1219.4 (a, 0.0)	1220.2 (a, 0.0)	1217.7 (a, 0.0)
1339.7 (b, 0.8)	1340.0 (a, 0.8)	1332.2 (a, 1.2)
1341.8 (a, 2.1)	1342.2 (a, 1.9)	1335.0 (a, 0.4)
1342.4 (a, 0.0)	1342.7 (a, 0.3)	1344.0 (a, 2.6)
1344.6 (b, 0.7)	1345.2 (a, 0.6)	1348.3 (a, 0.2)
1394.8 (b, 2.6)	1395.3 (a, 2.5)	1387.2 (a, 3.2)
1394.8 (a, 0.0)	1395.4 (a, 0.0)	1388.7 (a, 2.5)
1402.4 (a, 0.9)	1400.5 (a, 1.0)	1389.3 (a, 0.6)
1404.9 (b, 5.0)	1403.1 (a, 5.3)	1396.4 (a, 3.2)
1754.4 (a, 643.6)	1753.8 (a, 639.5)	1744.9 (a, 607.6)
3162.1 (a, 0.1)	3162.7 (a, 0.1)	3162.3 (a, 0.3)
3162.5 (b, 0.4)	3163.1 (a, 0.4)	3165.9 (a, 0.1)
3171.8 (b, 0.3)	3172.3 (a, 0.2)	3169.6 (a, 0.1)
3172.1 (a, 0.0)	3172.6 (a, 0.0)	3174.6 (a, 0.1)
3182.5 (b, 0.3)	3182.8 (a, 0.3)	3180.1 (a, 0.4)
3182.5 (a, 0.1)	3182.9 (a, 0.1)	3181.4 (a, 0.7)
3184.3 (b, 0.2)	3184.4 (a, 0.2)	3184.0 (a, 0.1)
3184.3 (a, 0.2)	3184.4 (a, 0.2)	3186.8 (a, 0.1)
3196.5 (b, 0.5)	3196.2 (a, 0.5)	3192.5 (a, 0.1)
3196.6 (a, 0.0)	3196.3 (a, 0.0)	3197.1 (a, 0.1)

Table S4. Theoretical harmonic vibrational frequencies (in cm^{-1}) for quintet and septet structures of $Cp_2Re_2(CO)$ using the BP86/SDD method (infrared intensities in parentheses are in km/mol).

ReI-Q (C_{2v})	**ReI-Q** (C_2) MPW1PW91	**ReI-H** (C_1)
14.1*i* (b_1, 2.2)	16.5*i* (b, 2.7)	31.9 (a, 0.6)
36.4 (a_2, 0.0)	36.5 (a, 0.0)	40.8 (a, 0.0)
50.0 (b_1, 0.0)	57.2 (b, 0.3)	54.6 (a, 0.4)
67.8 (a_2, 0.0)	84.6 (a, 1.6)	70.6 (a, 0.7)
87.3 (a_1, 2.2)	103.3 (a, 1.5)	81.7 (a, 0.1)
119.2 (b_2, 1.7)	104.6 (b, 1.3)	92.6 (a, 1.1)
192.3 (a_1, 0.0)	187.0 (a, 0.1)	180.6 (a, 2.4)
219.1 (b_2, 0.9)	212.9 (b, 4.8)	184.5 (a, 0.6)
272.2 (b_2, 4.6)	282.9 (b, 13.5)	222.4 (a, 5.5)
291.4 (a_1, 1.7)	286.1 (a, 2.8)	243.5 (a, 1.0)
302.6 (a_2, 0.0)	307.8 (b, 1.4)	255.2 (a, 3.0)
302.9 (b_1, 0.8)	330.7 (a, 0.0)	262.5 (a, 4.1)
305.5 (b_2, 6.7)	339.9 (b, 8.4)	281.5 (a, 0.5)
336.7 (a_1, 2.3)	366.5 (a, 3.4)	293.3 (a, 3.3)
463.1 (b_1, 3.2)	499.0 (b, 20.9)	432.3 (a, 5.3)
472.4 (b_2, 5.1)	507.1 (b, 19.2)	464.9 (a, 6.3)
502.9 (a_1, 1.6)	515.6 (a, 4.2)	484.9 (a, 3.8)
535.8 (a_2, 0.0)	577.7 (a, 0.0)	518.4 (a, 1.1)
542.1 (b_1, 0.1)	581.0 (b, 0.1)	532.7 (a, 0.8)
542.2 (b_2, 0.1)	585.8 (a, 0.0)	540.3 (a, 2.3)
544.0 (a_1, 0.0)	586.3 (b, 4.9)	544.7 (a, 0.1)
751.2 (a_2, 0.0)	805.2 (b, 18.8)	730.5 (a, 5.0)
762.8 (b_2, 24.1)	809.6 (a, 9.3)	743.6 (a, 12.7)
767.3 (b_1, 0.0)	817.9 (a, 8.0)	757.1 (a, 44.0)
769.1 (a_1, 16.3)	818.2 (b, 2.6)	769.5 (a, 66.6)
780.4 (b_2, 44.5)	819.9 (b, 50.5)	775.2 (a, 1.0)
786.5 (a_1, 3.1)	824.8 (a, 0.7)	782.4 (a, 12.0)
801.9 (a_2, 0.0)	836.5 (a, 0.8)	798.0 (a, 5.6)
806.0 (b_1, 0.6)	839.9 (b, 0.4)	800.3 (a, 1.9)
808.2 (b_2, 9.2)	845.0 (b, 9.0)	803.4 (a, 0.2)
809.9 (a_1, 1.7)	845.5 (a, 3.3)	805.6 (a, 0.5)
845.0 (a_2, 0.0)	888.8 (b, 9.2)	830.4 (a, 3.4)
846.0 (b_1, 0.6)	889.1 (a, 5.9)	832.2 (a, 2.6)
847.5 (b_2, 25.5)	903.6 (b, 3.6)	834.7 (a, 0.1)
848.1 (a_1, 13.5)	904.3 (a, 3.6)	846.8 (a, 1.6)
976.7 (b_2, 0.1)	1014.1 (a, 14.8)	974.1 (a, 17.7)
977.0 (a_2, 0.0)	1014.9 (b, 4.8)	978.5 (a, 8.2)
978.6 (a_1, 16.8)	1022.9 (a, 3.3)	983.5 (a, 9.6)

983.1 (b_1, 23.8)	1024.0 (b, 23.2)	993.0 (a, 12.7)
1035.5 (b_2, 0.3)	1072.3 (b, 0.6)	1034.0 (a, 1.1)
1036.0 (a_2, 0.0)	1072.8 (a, 1.5)	1035.2 (a, 0.4)
1036.3 (b_1, 0.1)	1076.7 (b, 1.5)	1036.7 (a, 0.6)
1036.7 (a_1, 0.6)	1077.5 (a, 0.2)	1042.0 (a, 0.9)
1084.8 (a_1, 1.1)	1133.5 (b, 29.7)	1088.3 (a, 10.6)
1085.0 (b_2, 27.9)	1134.0 (a, 0.6)	1094.0 (a, 4.5)
1220.8 (b_1, 0.0)	1272.2 (b, 0.0)	1218.7 (a, 0.0)
1220.8 (a_2, 0.0)	1272.2 (a, 0.0)	1223.1 (a, 0.0)
1337.7 (b_1, 0.0)	1395.8 (b, 2.3)	1341.3 (a, 0.2)
1341.3 (a_2, 0.0)	1397.5 (a, 1.3)	1342.9 (a, 0.5)
1345.7 (b_2, 3.7)	1419.8 (b, 2.1)	1344.1 (a, 1.4)
1347.8 (a_1, 2.6)	1422.0 (a, 0.3)	1350.5 (a, 3.1)
1386.9 (a_2, 0.0)	1454.7 (a, 2.4)	1389.2 (a, 3.5)
1389.8 (b_2, 1.6)	1454.9 (b, 0.7)	1390.7 (a, 1.6)
1390.7 (b_1, 6.9)	1458.3 (b, 7.6)	1397.2 (a, 4.0)
1391.8 (a_1, 6.1)	1458.8 (a, 3.7)	1411.2 (a, 2.5)
1725.3 (a_1, 545.9)	1828.9 (a, 719.7)	1701.4 (a, 562.8
3164.8 (a_2, 0.0)	3275.7 (a, 0.0)	3166.6 (a, 0.2)
3165.0 (b_1, 0.6)	3275.7 (b, 0.5)	3167.0 (a, 0.1)
3172.2 (b_2, 2.9)	3280.9 (b, 0.9)	3169.7 (a, 0.1)
3172.5 (a_1, 0.5)	3281.1 (a, 0.1)	3173.1 (a, 0.1)
3179.0 (b_2, 0.2)	3290.2 (a, 0.4)	3180.1 (a, 0.2)
3179.1 (a_1, 0.2)	3290.2 (b, 0.8)	3180.1 (a, 1.2)
3184.7 (a_2, 0.0)	3294.4 (b, 0.7)	3186.8 (a, 0.0)
3185.2 (b_1, 0.0)	3294.4 (a, 0.0)	3188.0 (a, 0.5)
3192.0 (b_2, 0.2)	3302.7 (b, 0.1)	3195.7 (a, 1.0)
3192.2 (a_1, 0.0)	3302.8 (a, 0.1)	3201.0 (a, 1.1)

Table S5. Theoretical harmonic vibrational frequencies (in cm^{-1}) for structures of $Cp_2W_2(CO)$ using the BP86/SDD method (infrared intensities in parentheses are in km/mol).

WI-S (C_1)	**WI-T$_1$** (C_1)	**WI-T$_2$** (C_1)	**WI-Q** (C_1)	**WI-H** (C_s)
43.3 (a, 0.5)	17.8 (a, 0.1)	30.8 (a, 0.3)	25.3 (a, 0.2)	19.4*i* (a", 0.8)
67.2 (a, 1.6)	20.0 (a, 0.2)	42.5 (a, 0.6)	35.2 (a, 0.6)	20.3 (a", 1.0)
75.9 (a, 0.3)	36.2 (a, 0.7)	49.9 (a, 0.6)	45.1 (a, 1.0)	33.6 (a", 0.8)
84.3 (a, 0.5)	47.1 (a, 1.1)	61.5 (a, 1.3)	53.0 (a, 0.2)	58.7 (a', 2.5)
91.9 (a, 0.5)	82.8 (a, 0.8)	69.9 (a, 0.3)	68.9 (a, 0.5)	75.1 (a", 0.1)
100.5 (a, 0.1)	104.8 (a, 1.4)	90.5 (a, 0.4)	98.2 (a, 0.1)	92.6 (a', 0.3)
120.2 (a, 1.4)	187.4 (a, 0.5)	105.5 (a, 0.1)	116.3 (a, 1.0)	150.8 (a', 0.0)
188.4 (a, 4.2)	254.2 (a, 1.0)	198.5 (a, 0.5)	181.7 (a, 1.1)	171.5 (a', 3.2)
198.8 (a, 4.0)	263.2 (a, 0.6)	222.0 (a, 3.4)	247.4 (a, 0.6)	274.6 (a', 5.1)
233.6 (a, 1.5)	273.8 (a, 3.5)	243.6 (a, 1.5)	264.7 (a, 20.4)	277.0 (a", 0.6)
274.2 (a, 2.2)	294.4 (a, 0.3)	278.8 (a, 1.8)	279.0 (a, 1.9)	283.0 (a', 4.5)
293.0 (a, 0.5)	299.8 (a, 2.7)	296.8 (a, 2.0)	291.9 (a, 5.4)	291.6 (a", 0.0)
315.8 (a, 6.6)	310.4 (a, 0.0)	324.5 (a, 4.0)	307.4 (a, 0.8)	304.8 (a', 4.2)
327.6 (a, 4.5)	332.1 (a, 3.6)	337.2 (a, 6.1)	341.0 (a, 2.6)	315.6 (a', 1.8)
415.7 (a, 12.0)	399.4 (a, 0.8)	442.8 (a, 5.8)	443.4 (a, 4.5)	432.6 (a", 0.2)
490.3 (a, 7.3)	508.5 (a, 17.5)	496.9 (a, 10.0)	495.8 (a, 7.4)	485.0 (a', 4.3)
499.8 (a, 4.8)	548.1 (a, 0.8)	510.7 (a, 1.9)	526.6 (a, 3.2)	506.5 (a', 0.9)
527.6 (a, 1.5)	549.3 (a, 0.1)	538.5 (a, 0.2)	539.7 (a, 0.0)	538.2 (a", 0.0)
546.9 (a, 4.6)	557.0 (a, 1.2)	542.4 (a, 0.5)	548.2 (a, 0.1)	544.6 (a", 0.1)
569.7 (a, 1.7)	563.2 (a, 0.6)	552.6 (a, 7.7)	549.6 (a, 0.5)	548.0 (a', 0.2)
579.8 (a, 4.6)	727.2 (a, 4.2)	569.2 (a, 4.2)	562.0 (a, 2.0)	560.0 (a', 0.9)
712.9 (a, 3.9)	740.4 (a, 8.2)	740.8 (a, 16.7)	742.4 (a, 20.7)	760.0 (a", 0.6)
741.9 (a, 38.2)	750.4 (a, 4.9)	743.5 (a, 43.6)	754.3 (a, 38.1)	760.5 (a', 83.8)
742.4 (a, 57.3)	759.8 (a, 67.4)	751.8 (a, 34.1)	754.6 (a, 17.0)	761.5 (a', 32.0)
753.6 (a, 3.0)	762.0 (a, 51.8)	753.8 (a, 20.6)	758.0 (a, 47.9)	761.6 (a", 0.5)
770.8 (a, 33.5)	769.4 (a, 5.6)	768.0 (a, 11.3)	761.0 (a, 26.0)	766.8 (a', 22.2)
782.7 (a, 2.5)	778.4 (a, 0.5)	790.8 (a, 3.2)	779.0 (a, 2.6)	770.5 (a', 5.6)
795.9 (a, 5.4)	797.3 (a, 0.3)	795.3 (a, 2.6)	797.1 (a, 5.4)	801.6 (a", 0.0)
800.3 (a, 4.1)	797.9 (a, 0.1)	796.8 (a, 1.9)	807.3 (a, 0.2)	806.0 (a", 0.1)
803.0 (a, 1.7)	808.8 (a, 0.3)	805.1 (a, 0.9)	808.6 (a, 1.4)	806.3 (a', 0.8)
809.6 (a, 0.1)	810.4 (a, 1.2)	810.4 (a, 2.8)	809.3 (a, 0.3)	809.1 (a', 0.0)
823.4 (a, 14.1)	823.5 (a, 0.1)	822.8 (a, 0.3)	829.7 (a, 0.7)	831.0 (a", 0.0)
828.6 (a, 10.6)	827.1 (a, 0.3)	834.8 (a, 0.4)	831.7 (a, 0.5)	836.6 (a', 0.7)
859.7 (a, 5.2)	839.2 (a, 2.4)	835.4 (a, 0.2)	839.3 (a, 0.8)	836.7 (a', 0.7)
864.8 (a, 4.6)	841.9 (a, 1.4)	851.5 (a, 1.1)	847.7 (a, 0.9)	837.5 (a", 0.0)
956.2 (a, 5.9)	974.4 (a, 25.4)	977.4 (a, 11.5)	978.6 (a, 8.9)	977.8 (a', 9.4)
966.7 (a, 15.2)	975.7 (a, 3.5)	979.4 (a, 14.9)	981.3 (a, 11.2)	983.0 (a', 12.4)
976.2 (a, 6.0)	980.3 (a, 17.5)	981.5 (a, 18.5)	984.6 (a, 14.7)	984.0 (a", 9.6)
984.9 (a, 6.9)	988.5 (a, 7.8)	983.3 (a, 6.2)	986.7 (a, 13.1)	987.4 (a", 15.1)

1024.5 (a, 2.4)	1031.0 (a, 0.6)	1036.3 (a, 0.4)	1034.5 (a, 0.3)	1033.9 (a", 0.1)
1033.5 (a, 0.6)	1037.4 (a, 0.0)	1037.7 (a, 0.8)	1035.5 (a, 0.0)	1036.3 (a", 0.2)
1039.1 (a, 2.3)	1040.2 (a, 1.6)	1038.2 (a, 1.2)	1037.5 (a, 0.8)	1037.5 (a', 0.6)
1040.0 (a, 7.3)	1040.9 (a, 0.8)	1040.2 (a, 0.8)	1039.5 (a, 0.2)	1039.1 (a', 0.6)
1071.5 (a, 12.4)	1084.4 (a, 19.8)	1087.3 (a, 16.5)	1088.9 (a, 12.4)	1087.3 (a', 18.7)
1085.8 (a, 10.2)	1091.5 (a, 18.9)	1089.4 (a, 13.3)	1092.8 (a, 8.6)	1092.7 (a', 10.9)
1212.8 (a, 0.0)	1216.4 (a, 0.0)	1218.0 (a, 0.0)	1217.4 (a, 0.0)	1218.2 (a", 0.0)
1221.2 (a, 0.0)	1219.2 (a, 0.0)	1219.1 (a, 0.0)	1220.4 (a, 0.0)	1219.9 (a", 0.0)
1292.4 (a, 1.0)	1334.9 (a, 0.7)	1336.9 (a, 0.6)	1341.3 (a, 0.5)	1346.1 (a', 1.7)
1315.1 (a, 7.2)	1349.3 (a, 89.4)	1344.5 (a, 0.4)	1348.9 (a, 0.2)	1350.3 (a', 0.7)
1327.8 (a, 11.5)	1352.3 (a, 2.7)	1347.2 (a, 6.4)	1352.7 (a, 0.4)	1351.2 (a", 0.0)
1340.5 (a, 2.5)	1353.6 (a, 79.0)	1351.4 (a, 1.8)	1354.5 (a, 1.1)	1353.3 (a", 0.4)
1383.6 (a, 4.7)	1358.6 (a, 33.1)	1394.4 (a, 1.4)	1394.4 (a, 3.3)	1391.1 (a', 1.4)
1389.0 (a, 1.0)	1387.3 (a, 3.0)	1396.9 (a, 6.7)	1399.0 (a, 2.3)	1395.4 (a', 2.9)
1419.1 (a, 3.3)	1389.1 (a, 0.7)	1402.7 (a, 0.9)	1400.1 (a, 2.6)	1395.6 (a", 3.3)
1425.1 (a, 7.2)	1399.7 (a, 2.6)	1403.8 (a, 2.8)	1405.7 (a, 0.7)	1401.0 (a", 2.8)
1773.0 (a, 794.7)	1403.9 (a, 4.1)	1760.9 (a, 728.6)	1761.9 (a, 668.9)	1701.2(a', 482.9)
3139.1 (a, 0.9)	3160.5 (a, 0.1)	3152.4 (a, 1.3)	3155.0 (a, 0.8)	3162.2 (a', 0.3)
3146.7 (a, 4.1)	3161.2 (a, 0.0)	3162.7 (a, 0.2)	3163.3 (a, 0.0)	3165.6 (a', 0.2)
3154.1 (a, 4.5)	3163.6 (a, 0.4)	3169.6 (a, 0.1)	3165.5 (a, 0.1)	3169.7 (a", 0.2)
3164.5 (a, 1.3)	3169.0 (a, 0.5)	3174.3 (a, 0.2)	3174.0 (a, 0.2)	3170.0 (a", 0.4)
3166.9 (a, 2.4)	3176.7 (a, 1.8)	3177.9 (a, 0.1)	3177.1 (a, 0.5)	3179.2 (a', 0.4)
3172.0 (a, 2.2)	3181.4 (a, 0.6)	3181.1 (a, 0.7)	3177.9 (a, 0.2)	3180.1 (a', 0.2)
3179.2 (a, 3.3)	3186.3 (a, 0.1)	3184.0 (a, 0.2)	3181.5 (a, 0.6)	3180.9 (a", 0.0)
3181.9 (a, 0.7)	3189.5 (a, 0.1)	3187.9 (a, 0.2)	3188.7 (a, 0.1)	3184.5 (a", 0.3)
3182.4 (a, 2.8)	3192.1 (a, 0.0)	3197.1 (a, 0.1)	3188.9 (a, 0.0)	3191.3 (a', 0.4)
3192.4 (a, 0.4)	3202.3 (a, 1.0)	3198.4 (a, 0.3)	3198.2 (a, 0.3)	3195.3 (a', 0.0)

Table S6. Theoretical harmonic vibrational frequencies (in cm^{-1}) for singlet and triplet structures of $Cp_2Ta_2(CO)$ using the BP86/SDD method (infrared intensities in parentheses are in km/mol).

TaI-S$_1$ (C_1)	**TaI-S$_2$** (C_s)	**TaI-T** (C_1)
30.9 (a, 0.1)	21.1*i* (a", 0.1)	35.8 (a, 0.2)
35.0 (a, 0.3)	55.4 (a', 1.0)	50.3 (a, 0.0)
53.6 (a, 0.2)	59.2 (a', 0.2)	62.2 (a, 0.3)
61.8 (a, 0.3)	75.0 (a", 0.0)	69.6 (a, 0.0)
78.1 (a, 0.2)	115.6 (a', 0.1)	81.8 (a, 0.1)
85.1 (a, 0.3)	117.3 (a", 0.4)	82.5 (a, 0.2)
183.1 (a, 0.4)	175.1 (a', 0.7)	171.6 (a, 0.1)
235.5 (a, 4.5)	204.8 (a", 5.4)	243.3 (a, 2.0)
248.6 (a, 0.8)	235.1 (a', 0.6)	246.1 (a, 0.5)
266.5 (a, 0.1)	252.7 (a", 24.7)	272.6 (a, 0.9)
272.2 (a, 0.4)	274.4 (a', 0.4)	280.1 (a, 0.3)
284.6 (a, 1.0)	277.7 (a", 11.3)	288.4 (a, 2.7)
302.0 (a, 1.2)	298.9 (a", 0.5)	311.7 (a, 3.1)
370.2 (a, 5.8)	309.3 (a', 11.9)	363.2 (a, 6.5)
426.6 (a, 3.0)	392.4 (a", 68.3)	447.2 (a, 2.5)
546.9 (a, 5.7)	402.1 (a', 8.1)	536.5 (a, 14.0)
555.6 (a, 4.2)	494.9 (a', 6.8)	556.6 (a, 0.5)
562.7 (a, 0.2)	536.5 (a', 0.7)	565.0 (a, 0.2)
567.2 (a, 2.7)	539.0 (a", 1.7)	570.0 (a, 1.0)
571.3 (a, 2.7)	555.2 (a', 0.1)	571.7 (a, 0.8)
706.4 (a, 1.0)	555.6 (a", 0.4)	703.6 (a, 2.6)
736.4 (a, 10.9)	731.8 (a", 15.4)	746.6 (a, 6.4)
745.2 (a, 1.8)	755.6 (a', 23.6)	751.7 (a, 27.0)
753.0 (a, 73.9)	760.1 (a", 45.8)	754.9 (a, 39.0)
758.1 (a, 8.3)	760.9 (a', 23.2)	758.0 (a, 59.6)
763.3 (a, 49.4)	764.9 (a", 7.3)	770.0 (a, 34.8)
769.7 (a, 66.3)	788.5 (a', 1.7)	772.6 (a, 49.5)
798.0 (a, 3.9)	792.1 (a", 2.5)	800.8 (a, 0.1)
808.1 (a, 8.1)	800.8 (a', 11.0)	812.7 (a, 0.6)
813.7 (a, 0.4)	805.7 (a", 1.9)	815.1 (a, 0.3)
817.1 (a, 0.1)	807.4 (a', 0.5)	817.1 (a, 0.0)
822.7 (a, 0.2)	822.4 (a", 0.6)	830.3 (a, 1.6)
830.6 (a, 4.0)	845.5 (a', 3.3)	836.6 (a, 0.8)
845.5 (a, 0.5)	846.3 (a", 0.8)	847.1 (a, 0.3)
853.8 (a, 1.0)	861.5 (a', 11.4)	847.8 (a, 0.3)
980.8 (a, 7.7)	975.8 (a", 12.7)	982.9 (a, 14.1)
983.8 (a, 15.5)	979.8 (a', 7.8)	985.6 (a, 12.9)
987.4 (a, 11.3)	981.9 (a", 3.1)	989.2 (a, 7.9)
991.5 (a, 8.0)	995.2 (a', 24.9)	993.2 (a, 12.9)

1035.8 (a, 1.7)	1031.2 (a", 0.0)	1037.0 (a, 0.0)
1040.4 (a, 1.4)	1038.0 (a", 0.6)	1039.2 (a, 0.8)
1041.6 (a, 2.0)	1039.0 (a', 0.3)	1041.6 (a, 1.2)
1042.2 (a, 1.7)	1046.4 (a', 1.1)	1043.7 (a, 0.4)
1093.2 (a, 9.2)	1093.6 (a", 12.6)	1094.3 (a, 9.0)
1097.5 (a, 5.4)	1094.9 (a', 22.8)	1097.9 (a, 5.4)
1219.1 (a, 0.0)	1216.7 (a", 0.0)	1220.9 (a, 0.0)
1222.5 (a, 0.0)	1222.0 (a', 0.0)	1222.0 (a, 0.0)
1261.8 (a, 192.6)	1347.2 (a", 4.0)	1260.4 (a, 231.9)
1348.8 (a, 2.0)	1350.3 (a', 0.4)	1347.0 (a, 0.1)
1349.6 (a, 1.3)	1361.7 (a", 1.0)	1353.1 (a, 0.2)
1350.2 (a, 7.2)	1365.2 (a', 5.1)	1358.3 (a, 0.9)
1360.2 (a, 2.9)	1398.1 (a", 0.4)	1360.3 (a, 2.4)
1398.5 (a, 3.7)	1398.9 (a', 1.1)	1398.9 (a, 2.2)
1398.9 (a, 4.6)	1406.3 (a", 0.0)	1404.9 (a, 2.1)
1411.4 (a, 2.2)	1409.3 (a', 3.8)	1407.3 (a, 1.3)
1417.5 (a, 4.9)	1618.4 (a', 494.1)	1415.1 (a, 1.1)
3151.1 (a, 0.9)	3144.5 (a", 0.2)	3150.5 (a, 0.7)
3152.1 (a, 0.2)	3144.5 (a', 0.6)	3153.9 (a, 0.0)
3158.9 (a, 2.3)	3160.8 (a", 0.0)	3161.7 (a, 0.9)
3164.0 (a, 0.8)	3160.9 (a', 0.5)	3165.1 (a, 0.6)
3172.1 (a, 0.9)	3182.1 (a", 0.7)	3171.3 (a, 1.0)
3172.5 (a, 1.4)	3182.3 (a', 0.8)	3173.7 (a, 0.6)
3179.9 (a, 1.3)	3185.4 (a', 0.9)	3175.2 (a, 0.6)
3180.3 (a, 0.3)	3186.3 (a", 0.0)	3182.8 (a, 0.2)
3193.0 (a, 1.2)	3205.7 (a", 0.2)	3191.9 (a, 1.0)
3196.6 (a, 0.9)	3205.8 (a', 4.4)	3199.1 (a, 0.8)

Table S7. Theoretical harmonic vibrational frequencies (in cm^{-1}) for quintet and septet structures of $Cp_2Ta_2(CO)$ using the BP86/SDD method (infrared intensities in parentheses are in km/mol).

TaI-Q (C_2)	**TaI-H** (C_2)	**TaI-H** (C_1) MPW1PW91
34.7 (b, 2.5)	8.8 (b, 0.5)	19.8 (a, 0.7)
36.0 (a, 0.5)	19.0 (a, 0.1)	24.5 (a, 0.3)
44.6 (b, 0.1)	27.2 (b, 0.8)	29.5 (a, 0.9)
51.3 (a, 0.0)	46.8 (a, 0.7)	38.8 (a, 0.9)
63.1 (b, 0.7)	61.3 (b, 0.7)	61.8 (a, 1.2)
87.8 (a, 0.0)	88.9 (a, 0.3)	79.0 (a, 0.3)
172.7 (a, 0.0)	133.2 (a, 0.0)	117.8 (a, 0.2)
176.1 (b, 0.3)	192.6 (b, 0.5)	123.0 (a, 0.1)
247.5 (a, 0.4)	261.9 (b, 1.2)	267.2 (a, 1.2)
247.7 (b, 8.3)	278.3 (a, 0.0)	291.6 (a, 2.3)
255.6 (b, 0.5)	287.1 (b, 6.3)	312.5 (a, 6.2)
265.1 (a, 0.9)	300.8 (b, 3.2)	318.2 (a, 2.1)
283.0 (b, 0.7)	301.6 (a, 0.1)	325.4 (a, 1.7)
290.3 (a, 0.0)	316.9 (a, 1.2)	331.2 (a, 0.1)
299.3 (b, 2.5)	344.1 (b, 24.3)	375.8 (a, 2.0)
385.2 (a, 0.6)	399.7 (a, 0.0)	443.7 (a, 10.4)
414.9 (b, 8.4)	412.6 (b, 5.1)	524.5 (a, 22.7)
550.6 (b, 1.0)	555.5 (b, 1.3)	589.1 (a, 0.9)
551.5 (a, 0.6)	557.6 (a, 0.1)	592.2 (a, 2.0)
556.5 (a, 1.1)	562.1 (b, 0.8)	599.4 (a, 0.2)
560.4 (b, 1.3)	565.2 (a, 0.1)	604.2 (a, 0.1)
745.9 (b, 11.1)	743.5 (b, 31.8)	795.3 (a, 60.2)
747.3 (a, 4.8)	745.8 (a, 0.1)	797.3 (a, 27.1)
752.5 (b, 80.6)	753.5 (b, 30.7)	799.3 (a, 38.5)
754.9 (a, 20.4)	757.6 (a, 2.7)	801.0 (a, 44.4)
772.1 (a, 15.3)	761.7 (b, 93.8)	804.8 (a, 13.0)
773.7 (b, 41.2)	762.9 (a, 5.7)	811.0 (a, 5.1)
806.4 (a, 3.4)	800.0 (b, 3.4)	841.6 (a, 3.5)
807.3 (b, 1.8)	802.3 (a, 0.0)	842.8 (a, 0.5)
808.5 (b, 0.0)	809.4 (b, 3.5)	845.3 (a, 0.3)
810.4 (a, 0.2)	812.6 (a, 0.0)	846.3 (a, 0.1)
831.9 (a, 0.0)	827.4 (b, 0.1)	880.8 (a, 0.8)
832.0 (b, 0.4)	828.0 (a, 0.0)	885.5 (a, 0.6)
843.7 (a, 3.7)	840.2 (b, 0.7)	889.5 (a, 0.2)
846.6 (b, 3.8)	840.7 (a, 0.7)	891.6 (a, 0.6)
984.2 (b, 12.4)	978.0 (b, 1.5)	1023.9 (a, 31.9)
984.8 (a, 16.8)	979.9 (a, 23.1)	1024.6 (a, 9.8)
988.5 (b, 21.0)	983.2 (b, 36.5)	1026.5 (a, 13.9)

990.7 (a, 8.1)	984.5 (a, 0.4)	1029.1 (a, 12.9)
1036.1 (b, 0.1)	1034.9 (b, 0.2)	1075.0 (a, 0.5)
1038.0 (a, 0.3)	1035.8 (a, 0.1)	1077.3 (a, 0.2)
1043.2 (b, 1.0)	1039.5 (b, 0.4)	1077.5 (a, 0.6)
1043.5 (a, 0.0)	1040.8 (a, 1.1)	1077.7 (a, 0.1)
1095.6 (b, 21.2)	1085.8 (b, 31.7)	1139.0 (a, 13.5)
1096.1 (a, 3.5)	1086.4 (a, 0.1)	1139.5 (a, 9.6)
1219.4 (b, 0.0)	1217.8 (b, 0.0)	1271.1 (a, 0.0)
1220.0 (a, 0.0)	1217.8 (a, 0.0)	1273.4 (a, 0.0)
1352.4 (b, 1.5)	1341.2 (b, 2.4)	1412.5 (a, 2.1)
1353.8 (a, 2.1)	1342.3 (a, 0.2)	1414.9 (a, 0.0)
1359.5 (a, 0.0)	1352.7 (b, 1.2)	1419.8 (a, 1.9)
1360.3 (b, 2.3)	1353.8 (a, 1.6)	1422.2 (a, 1.3)
1400.3 (a, 0.9)	1391.9 (b, 0.5)	1461.3 (a, 1.3)
1401.0 (b, 3.1)	1393.8 (a, 1.9)	1462.2 (a, 1.0)
1405.7 (b, 2.1)	1397.3 (b, 0.2)	1467.2 (a, 1.9)
1406.6 (a, 0.3)	1398.3 (a, 0.8)	1468.1 (a, 3.0)
1654.9 (a, 463.7)	1652.1 (a, 408.5)	1835.1 (a, 695.8)
3156.8 (a, 0.0)	3156.4 (b, 1.2)	3264.8 (a, 2.4)
3156.9 (b, 0.5)	3156.9 (a, 0.1)	3266.6 (a, 0.5)
3166.1 (b, 0.5)	3164.7 (b, 0.6)	3274.0 (a, 0.4)
3166.2 (a, 0.1)	3164.8 (a, 0.0)	3275.4 (a, 0.2)
3175.0 (b, 0.5)	3175.4 (b, 0.1)	3284.1 (a, 0.8)
3175.2 (a, 0.0)	3175.5 (a, 0.3)	3284.3 (a, 0.4)
3182.5 (a, 0.2)	3176.6 (b, 0.4)	3286.0 (a, 1.5)
3182.5 (b, 0.4)	3176.8 (a, 0.2)	3288.5 (a, 0.4)
3195.6 (a, 0.0)	3190.1 (b, 0.5)	3297.6 (a, 0.5)
3196.0 (b, 0.7)	3190.2 (a, 0.0)	3298.7 (a, 0.0)

Table S8. Theoretical harmonic vibrational frequencies (in cm^{-1}) for structures of Cp_2M-M(CO) (M = Os, Re) using the BP86/SDD method (infrared intensities in parentheses are in km/mol).

OsII-T (C_s)	**ReII-T** (C_1)	**ReII-Q** (C_{2v})	**ReII-H** (C_s)
11.9 (a", 1.0)	22.2 (a, 0.5)	7.2 (b_1, 0.4)	16.6 (a", 0.1)
52.3 (a", 0.0)	66.6 (a, 0.5)	28.6 (b_1, 0.2)	39.4 (a", 0.1)
52.9 (a', 0.3)	109.7 (a, 0.3)	28.6 (b_2, 0.4)	54.5 (a", 0.0)
65.6 (a', 0.3)	133.7 (a, 0.9)	49.4 (a_2, 0.0)	57.9 (a', 0.7)
90.1 (a", 0.0)	136.1 (a, 3.9)	70.3 (b_2, 0.4)	89.1 (a', 0.9)
117.5 (a', 0.6)	154.3 (a, 1.2)	118.0 (a_1, 0.0)	122.2 (a', 0.8)
140.6 (a", 5.1)	175.6 (a, 2.3)	138.8 (b_1, 5.4)	126.8 (a", 5.0)
170.4 (a', 24.0)	199.9 (a, 12.3)	163.4 (a_1, 5.1)	138.5 (a", 0.0)
342.7 (a', 3.8)	333.8 (a, 19.6)	318.5 (a_1, 2.6)	163.9 (a', 11.7)
347.3 (a', 10.2)	336.0 (a, 19.9)	346.3 (b_2, 9.6)	269.4 (a', 1.7)
373.8 (a', 2.2)	359.9 (a, 3.2)	349.5 (b_1, 8.8)	309.2 (a', 0.5)
378.3 (a", 3.2)	371.0 (a, 0.6)	356.8 (a_2, 0.0)	333.1 (a', 6.5)
384.9 (a", 10.2)	389.6 (a, 8.1)	377.7 (b_1, 1.0)	348.5 (a", 1.4)
404.1 (a', 27.2)	406.6 (a, 1.0)	377.8 (b_2, 0.1)	364.9 (a", 7.9)
433.5 (a", 0.5)	426.0 (a, 1.4)	392.8 (a_1, 5.2)	365.5 (a', 3.7)
453.2 (a', 1.7)	475.9 (a, 10.1)	437.1 (b_2, 2.2)	384.5 (a', 26.8)
538.0 (a', 2.3)	489.1 (a, 8.8)	482.8 (a_1, 2.7)	405.7 (a', 6.0)
553.1 (a", 0.1)	541.0 (a, 0.0)	548.6 (a_2, 0.0)	535.8 (a", 0.0)
554.7 (a', 2.1)	545.7 (a, 0.0)	554.4 (a_1, 1.2)	549.2 (a', 0.4)
555.1 (a", 0.0)	574.0 (a, 11.0)	558.1 (b_1, 0.1)	550.6 (a", 0.4)
566.0 (a', 0.3)	589.7 (a, 6.9)	561.0 (b_2, 0.6)	554.5 (a', 0.2)
759.9 (a', 9.1)	742.0 (a, 3.9)	762.1 (a_2, 0.0)	755.8 (a", 0.0)
776.2 (a", 0.1)	745.6 (a, 11.0)	766.2 (a_2, 0.0)	766.0 (a', 10.0)
779.0 (a', 29.1)	767.1 (a, 2.1)	767.9 (b_2, 8.2)	771.7 (a", 0.2)
780.7 (a", 0.7)	773.3 (a, 0.5)	785.5 (b_2, 10.5)	787.5 (a', 12.2)
797.2 (a', 36.1)	780.1 (a, 8.7)	792.3 (a_1, 6.1)	790.7 (a", 3.5)
799.2 (a', 30.4)	785.6 (a, 34.2)	792.9 (b_1, 1.0)	791.9 (a', 39.8)
804.6 (a", 3.1)	797.3 (a, 8.3)	795.3 (b_2, 54.3)	792.6 (a", 0.0)
807.8 (a', 2.1)	800.5 (a, 2.8)	799.5 (a_1, 7.5)	802.7 (a', 15.4)
814.0 (a", 3.4)	804.4 (a, 3.8)	809.3 (b_1, 3.3)	809.7 (a', 0.3)
831.3 (a', 5.0)	818.3 (a, 0.2)	811.5 (a_1, 1.5)	815.5 (a', 10.2)
841.8 (a", 0.0)	827.0 (a, 0.4)	833.3 (b_2, 3.7)	839.6 (a', 17.5)
842.5 (a', 3.0)	836.6 (a, 0.4)	839.4 (a_2, 0.0)	843.0 (a", 0.5)
851.6 (a", 0.2)	841.4 (a, 0.1)	846.2 (a_1, 0.0)	846.4 (a', 4.6)
860.3 (a", 0.3)	845.9 (a, 0.2)	852.4 (b_1, 0.8)	851.4 (a", 1.1)
902.8 (a', 12.3)	940.8 (a, 0.2)	958.9 (b_2, 0.1)	958.0 (a', 0.8)
960.4 (a', 1.6)	943.8 (a, 3.1)	966.6 (a_1, 8.0)	965.9 (a', 9.0)
968.3 (a", 6.2)	975.4 (a, 40.1)	972.8 (a_2, 0.0)	971.5 (a", 0.0)
970.2 (a', 2.9)	1000.8 (a, 0.5)	981.9 (b_1, 19.8)	982.5 (a", 22.6)

1004.2 (a", 5.9)	1008.3 (a, 24.5)	1025.0 (b_2, 0.7)	1024.5 (a", 0.0)
1021.9 (a", 3.4)	1014.8 (a, 18.9)	1025.9 (a_2, 0.0)	1025.0 (a', 1.2)
1025.6 (a', 0.1)	1028.2 (a, 0.9)	1028.4 (a_1, 2.7)	1029.5 (a', 1.6)
1035.7 (a', 0.6)	1034.2 (a, 0.6)	1032.4 (b_1, 0.0)	1033.4 (a", 0.0)
1065.5 (a', 21.8)	1058.6 (a, 22.9)	1079.4 (b_2, 30.5)	1078.9 (a', 20.7)
1080.0 (a', 15.2)	1065.3 (a, 17.8)	1079.5 (a_1, 4.5)	1079.1 (a', 7.3)
1176.8 (a", 0.0)	1172.6 (a, 0.1)	1210.2 (b_1, 0.3)	1209.4 (a", 0.0)
1208.0 (a", 0.0)	1175.6 (a, 0.4)	1210.9 (a_2, 0.0)	1210.2 (a", 0.4)
1289.3 (a", 0.2)	1268.5 (a, 0.1)	1338.8 (a_2, 0.0)	1335.9 (a", 0.0)
1336.2 (a', 2.7)	1281.8 (a, 0.6)	1340.7 (b_2, 0.1)	1340.2 (a', 0.4)
1340.3 (a", 0.0)	1329.6 (a, 0.8)	1352.9 (a_1, 2.0)	1353.4 (a", 0.0)
1355.6 (a', 6.4)	1339.4 (a, 1.6)	1353.9 (b_1, 0.1)	1353.6 (a', 0.8)
1369.7 (a', 5.4)	1357.5 (a, 0.0)	1373.2 (b_2, 0.2)	1370.5 (a', 0.6)
1372.7 (a", 1.4)	1364.4 (a, 4.8)	1374.1 (a_1, 5.5)	1372.7 (a', 2.8)
1376.0 (a', 5.8)	1370.7 (a, 1.8)	1380.9 (a_2, 0.0)	1381.1 (a", 0.7)
1380.9 (a", 2.2)	1374.0 (a, 0.8)	1383.2 (b_1, 8.9)	1383.7 (a", 7.2)
1892.5 (a', 1332.1)	1862.9 (a, 1528.8)	1854.5 (a_1, 1415.8)	1789.0 (a', 1158.5)
2597.8 (a', 0.1)	2300.1 (a, 13.5)	3138.9 (b_1, 0.1)	3151.1 (a", 0.0)
3098.7 (a', 3.4)	2362.8 (a, 12.9)	3139.0 (a_2, 0.0)	3155.0 (a", 0.4)
3164.9 (a", 0.8)	3165.1 (a, 0.5)	3148.2 (b_2, 0.0)	3158.4 (a', 0.1)
3170.1 (a", 0.8)	3165.7 (a, 0.9)	3149.4 (a_1, 3.8)	3162.9 (a', 2.9)
3174.3 (a', 3.0)	3174.1 (a, 0.9)	3163.9 (b_2, 0.1)	3163.2 (a', 1.2)
3178.8 (a', 2.9)	3175.3 (a, 1.4)	3166.2 (a_1, 2.5)	3167.4 (a', 4.8)
3185.9 (a", 0.3)	3183.9 (a, 0.7)	3179.5 (b_1, 6.5)	3179.2 (a", 2.0)
3187.2 (a", 1.0)	3187.5 (a, 1.3)	3180.1 (a_2, 0.0)	3181.0 (a", 3.9)
3189.0 (a', 1.6)	3188.1 (a, 0.6)	3185.2 (a_1, 4.1)	3184.4 (a', 5.2)
3191.7 (a', 1.2)	3192.7 (a, 0.4)	3185.8 (b_2, 1.1)	3186.9 (a', 2.5)

Table S9. Theoretical harmonic vibrational frequencies (in cm^{-1}) for structures of Cp_2W-W(CO) using the BP86/SDD method (infrared intensities in parentheses are in km/mol).

WII-T (C_s)	**WII-Q** (C_s) MPW1PW91/SDD	**WII-Q** (C_1)
23.5 (a", 2.0)	35.7 (a", 1.6)	37.5 (a, 0.4)
28.1 (a', 1.4)	48.8 (a', 0.1)	48.7 (a, 0.2)
59.2 (a", 1.9)	63.6 (a', 0.0)	54.5 (a, 0.2)
60.3 (a', 1.1)	73.1 (a", 1.5)	61.3 (a, 0.5)
94.8 (a", 1.5)	76.7 (a", 1.1)	89.3 (a, 1.2)
110.8 (a', 1.2)	110.0 (a', 0.7)	110.5 (a, 1.2)
122.6 (a', 6.5)	128.3 (a', 8.8)	116.0 (a, 3.4)
188.3 (a', 0.2)	205.8 (a', 2.9)	183.2 (a, 1.0)
289.6 (a', 0.4)	313.0 (a', 4.9)	294.3 (a, 3.6)
308.8 (a", 3.1)	339.0 (a", 7.6)	316.3 (a, 3.5)
314.0 (a', 7.2)	346.7 (a", 2.4)	326.3 (a, 7.5)
328.6 (a", 0.2)	359.0 (a', 36.0)	331.8 (a, 0.7)
339.5 (a", 2.9)	361.8 (a", 0.6)	342.7 (a, 1.5)
352.3 (a', 2.1)	368.1 (a', 3.9)	350.0 (a, 27.6)
409.4 (a", 3.5)	382.1 (a", 0.7)	372.0 (a, 6.9)
409.6 (a', 3.7)	387.0 (a', 7.3)	388.0 (a, 6.7)
547.5 (a', 1.3)	426.2 (a', 14.9)	449.7 (a, 20.6)
547.6 (a", 0.9)	584.8 (a", 0.9)	538.7 (a, 1.1)
549.4 (a', 1.3)	588.2 (a', 0.1)	550.1 (a, 1.5)
555.2 (a", 1.1)	592.1 (a", 0.2)	560.5 (a, 0.5)
564.4 (a', 0.7)	599.4 (a', 0.7)	561.0 (a, 0.5)
735.2 (a", 10.7)	769.9 (a", 2.4)	720.2 (a, 5.6)
745.2 (a", 10.2)	781.7 (a", 23.2)	740.6 (a, 11.0)
777.7 (a", 32.0)	805.8 (a', 1.0)	752.8 (a, 11.4)
779.5 (a', 9.7)	810.3 (a", 32.0)	754.0 (a, 51.4)
784.3 (a', 13.9)	819.0 (a', 4.4)	771.8 (a, 15.7)
786.7 (a', 3.4)	824.6 (a', 0.2)	779.7 (a, 15.8)
792.1 (a", 42.8)	829.0 (a", 11.2)	782.2 (a, 0.1)
800.6 (a', 3.5)	831.4 (a', 17.6)	796.6 (a, 13.6)
806.6 (a", 27.3)	838.9 (a", 23.2)	799.7 (a, 9.7)
814.7 (a', 0.5)	844.0 (a', 0.9)	806.7 (a, 19.8)
825.3 (a", 20.1)	874.1 (a", 23.4)	826.4 (a, 3.9)
836.4 (a', 6.8)	883.6 (a', 5.4)	832.2 (a, 3.4)
855.0 (a", 7.5)	887.8 (a", 3.1)	837.0 (a, 5.3)
859.6 (a', 10.5)	894.3 (a', 6.5)	841.3 (a, 4.2)
963.6 (a", 1.4)	1003.3 (a", 0.7)	947.4 (a, 7.4)
965.9 (a', 15.3)	1004.9 (a', 17.8)	957.3 (a, 9.2)
980.5 (a", 1.4)	1016.8 (a", 0.0)	969.8 (a, 15.6)

987.2 (a', 18.7)	1025.4 (a', 25.1)	983.9 (a, 13.4)
1026.7 (a", 0.0)	1066.8 (a", 0.0)	1018.3 (a, 11.0)
1034.6 (a', 0.1)	1072.0 (a', 1.8)	1030.3 (a, 2.9)
1040.8 (a", 0.2)	1072.1 (a", 0.1)	1036.1 (a, 5.8)
1042.5 (a', 0.4)	1074.9 (a', 0.1)	1038.9 (a, 1.1)
1081.2 (a", 16.9)	1122.3 (a", 25.1)	1066.1 (a, 24.9)
1081.7 (a', 4.2)	1122.7 (a', 8.7)	1083.1 (a, 13.4)
1215.7 (a", 0.0)	1267.9 (a', 0.1)	1201.5 (a, 0.2)
1216.2 (a', 0.0)	1268.4 (a", 0.0)	1214.9 (a, 0.1)
1329.3 (a", 0.7)	1399.8 (a", 0.1)	1304.7 (a, 2.2)
1338.5 (a', 0.0)	1409.6 (a", 0.0)	1343.7 (a, 0.1)
1345.5 (a", 0.0)	1412.4 (a', 0.4)	1348.4 (a, 2.3)
1354.0 (a', 6.2)	1418.5 (a', 0.8)	1354.3 (a, 1.0)
1383.9 (a", 5.3)	1439.9 (a", 4.3)	1369.8 (a, 0.2)
1384.5 (a', 2.9)	1440.1 (a', 1.3)	1381.5 (a, 2.9)
1398.0 (a", 0.0)	1453.3 (a", 0.1)	1383.9 (a, 1.3)
1398.1 (a', 2.7)	1454.8 (a', 6.0)	1392.1 (a, 4.0)
1804.9 (a', 869.9)	1991.2 (a', 1743.7)	1826.1(a, 1766.9)
3145.5 (a", 0.3)	3267.4 (a", 0.1)	3076.9 (a, 1.2)
3145.5 (a', 4.9)	3267.7 (a', 1.4)	3164.2 (a, 0.8)
3167.7 (a", 0.9)	3275.5 (a", 1.2)	3165.6 (a, 3.1)
3171.1 (a', 0.4)	3277.5 (a', 0.3)	3172.1 (a, 1.0)
3181.0 (a', 2.9)	3279.6 (a", 0.1)	3173.4 (a, 1.3)
3181.2 (a", 0.0)	3282.0 (a', 2.7)	3180.2 (a, 0.2)
3183.3 (a', 4.2)	3296.0 (a', 0.7)	3182.5 (a, 0.3)
3183.6 (a", 0.1)	3296.2 (a", 0.0)	3184.0 (a, 0.8)
3193.7 (a', 0.6)	3302.3 (a', 0.7)	3188.0 (a, 0.0)
3194.3 (a", 0.0)	3303.0 (a", 0.0)	3192.8 (a, 0.1)

Table S10. Theoretical harmonic vibrational frequencies (in cm^{-1}) for structures of Cp_2Ta-Ta(CO) using the BP86/SDD method (infrared intensities in parentheses are in km/mol).

TaII-T (C_s)	**TaII-Q** (C_s)	**TaII-H** (C_s)
4.9 (a", 0.7)	23.3 (a", 1.0)	25.3 (a', 0.1)
47.8 (a', 0.5)	42.4 (a", 0.1)	27.0 (a", 0.9)
48.3 (a", 0.0)	53.3 (a', 0.8)	39.3 (a", 0.1)
66.2 (a", 1.5)	66.7 (a", 1.2)	42.4 (a', 0.8)
77.5 (a', 1.1)	77.3 (a', 0.8)	57.1 (a', 1.0)
88.3 (a", 1.0)	112.1 (a", 0.7)	64.1 (a", 1.8)
128.8 (a', 0.6)	133.2 (a', 0.4)	81.1 (a', 0.1)
172.1 (a', 1.0)	186.1 (a', 1.2)	148.5 (a', 2.2)
273.6 (a', 0.3)	271.8 (a', 0.8)	266.5 (a', 0.0)
300.0 (a', 0.4)	288.9 (a", 3.0)	303.8 (a', 1.8)
301.0 (a", 0.5)	297.6 (a', 0.3)	304.2 (a", 0.0)
306.8 (a", 0.7)	307.9 (a", 0.3)	309.4 (a', 4.5)
314.1 (a', 4.5)	312.9 (a', 5.5)	309.4 (a", 0.0)
328.3 (a", 0.1)	336.9 (a", 0.0)	320.4 (a", 0.1)
342.0 (a', 4.5)	343.3 (a', 2.5)	335.0 (a", 0.0)
370.8 (a', 0.0)	371.5 (a', 0.7)	342.2 (a', 0.9)
418.6 (a', 0.1)	419.9 (a', 0.1)	407.6 (a', 0.6)
543.0 (a", 0.1)	542.9 (a", 0.9)	560.4 (a", 0.0)
545.1 (a', 0.9)	543.5 (a', 0.6)	561.8 (a', 0.3)
574.8 (a", 0.0)	568.6 (a', 0.2)	565.1 (a", 1.1)
578.9 (a', 1.0)	571.8 (a", 0.0)	570.4 (a', 0.1)
666.0 (a", 1.5)	667.9 (a", 2.7)	751.1 (a", 19.8)
678.1 (a', 15.3)	688.4 (a', 14.9)	759.9 (a', 2.5)
724.4 (a", 0.6)	716.7 (a", 1.9)	766.0 (a", 2.1)
736.4 (a', 40.2)	742.8 (a', 55.8)	769.8 (a", 143.8)
749.6 (a", 1.0)	753.2 (a", 0.2)	772.6 (a', 1.1)
760.4 (a', 59.7)	763.5 (a', 5.8)	779.3 (a', 12.9)
763.4 (a', 18.8)	766.9 (a', 49.4)	796.7 (a", 5.3)
796.8 (a', 1.9)	799.5 (a', 5.7)	803.5 (a', 1.1)
807.0 (a", 0.0)	802.3 (a", 0.2)	810.9 (a", 5.1)
815.3 (a", 1.0)	816.2 (a', 3.1)	815.2 (a', 0.2)
816.1 (a', 2.0)	816.4 (a", 2.2)	829.6 (a", 0.4)
820.4 (a', 1.5)	827.1 (a', 5.2)	838.0 (a', 0.9)
836.1 (a", 1.8)	835.2 (a", 0.9)	842.8 (a", 0.6)
837.3 (a', 0.4)	839.4 (a', 1.7)	846.7 (a', 0.7)
939.2 (a', 6.1)	938.0 (a', 2.3)	974.4 (a", 2.2)
954.9 (a", 15.6)	950.2 (a", 21.0)	977.6 (a', 22.3)
981.4 (a', 8.7)	980.5 (a', 8.7)	980.1 (a", 0.1)
987.9 (a", 16.1)	989.4 (a", 16.9)	982.1 (a', 17.6)

1019.2 (a', 7.8)	1015.1 (a', 12.2)	1032.1 (a", 2.2)
1031.3 (a", 1.4)	1034.0 (a", 1.5)	1032.8 (a', 5.8)
1037.8 (a", 0.4)	1038.5 (a", 0.9)	1035.4 (a", 1.1)
1045.2 (a', 1.3)	1041.9 (a', 0.8)	1041.4 (a', 1.4)
1055.5 (a', 33.0)	1055.0 (a', 29.3)	1085.0 (a", 18.1)
1092.9 (a', 8.9)	1092.9 (a', 12.2)	1085.2 (a', 6.8)
1200.7 (a", 0.5)	1204.0 (a", 1.2)	1215.3 (a", 0.1)
1218.7 (a", 0.0)	1219.5 (a", 0.0)	1216.1 (a', 0.1)
1296.9 (a', 0.4)	1286.3 (a', 3.2)	1340.2 (a", 0.8)
1326.9 (a", 4.3)	1324.9 (a", 6.4)	1343.0 (a', 0.7)
1353.8 (a", 0.3)	1355.3 (a', 0.3)	1352.3 (a", 0.1)
1357.8 (a', 0.3)	1356.9 (a", 0.2)	1357.8 (a', 1.9)
1372.2 (a', 1.2)	1373.3 (a', 1.2)	1390.9 (a", 0.5)
1381.5 (a", 0.5)	1387.6 (a", 0.0)	1391.7 (a', 3.4)
1396.6 (a', 1.1)	1395.8 (a', 0.7)	1397.1 (a', 3.0)
1402.0 (a", 1.3)	1403.1 (a", 1.2)	1397.3 (a", 0.0)
1851.6 (a', 1035.7)	1850.1 (a', 1057.7)	1845.2 (a', 1032.7)
3087.6 (a", 2.4)	3059.4 (a", 0.8)	3117.5 (a', 9.9)
3094.8 (a', 6.3)	3065.3 (a', 12.7)	3118.0 (a", 1.3)
3156.3 (a', 0.4)	3154.8 (a', 0.6)	3160.0 (a", 0.1)
3159.8 (a', 1.7)	3158.2 (a', 0.4)	3160.8 (a', 0.3)
3169.2 (a", 1.5)	3167.6 (a", 1.2)	3167.3 (a", 0.0)
3176.2 (a', 1.5)	3172.7 (a", 0.4)	3168.0 (a', 2.2)
3176.9 (a", 0.1)	3176.0 (a', 2.0)	3174.1 (a", 0.0)
3182.8 (a', 0.1)	3178.4 (a', 0.6)	3174.2 (a', 0.5)
3186.1 (a", 0.0)	3181.9 (a", 0.3)	3182.2 (a", 0.0)
3198.1 (a', 0.6)	3193.9 (a', 0.4)	3182.3 (a', 0.8)

Table S11. Theoretical Cartesian coordinates (in Å) for the structure **OsI-S** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	3.287123	0.909520
2	6	0.951433	3.385090	-0.123626
3	6	0.350707	2.957239	-1.360264
4	6	-1.015624	2.601811	-1.079346
5	6	-1.210394	2.754249	0.344325
6	1	0.175126	3.477327	1.960868
7	1	1.990184	3.668411	0.001068
8	1	0.822000	2.970737	-2.334619
9	1	-1.767122	2.305113	-1.799035
10	1	-2.133750	2.572914	0.879469
11	6	1.015624	-2.601811	-1.079346
12	6	1.210394	-2.754249	0.344325
13	6	-0.350707	-2.957239	-1.360264
14	1	1.767122	-2.305113	-1.799035
15	6	0.000000	-3.287123	0.909520
16	1	2.133750	-2.572914	0.879469
17	6	-0.951433	-3.385090	-0.123626
18	1	-0.822000	-2.970737	-2.334619
19	1	-0.175126	-3.477327	1.960868
20	1	-1.990184	-3.668411	0.001068
21	6	0.000000	0.000000	1.600686
22	8	0.000000	0.000000	2.784191
23	76	0.203303	1.136222	-0.089345
24	76	-0.203303	-1.136222	-0.089345

Table S12. Theoretical Cartesian coordinates (in Å) for the structure **OsI-T** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	3.166413	-1.241458
2	6	-1.235002	2.887514	-0.559810
3	6	-0.938856	2.817386	0.843713
4	6	0.475372	3.044447	1.018332
5	6	1.047768	3.268990	-0.273746
6	1	0.121960	3.246582	-2.315080
7	1	-2.210109	2.781834	-1.016453
8	1	-1.648691	2.618316	1.636355
9	1	1.005525	3.038516	1.962049
10	1	2.094284	3.451210	-0.483283
11	6	-1.047768	-3.268990	-0.273746
12	6	0.000000	-3.166413	-1.241458
13	6	-0.475372	-3.044447	1.018332
14	1	-2.094284	-3.451210	-0.483283
15	6	1.235002	-2.887514	-0.559810
16	1	-0.121960	-3.246582	-2.315080
17	6	0.938856	-2.817386	0.843713
18	1	-1.005525	-3.038516	1.962049
19	1	2.210109	-2.781834	-1.016453
20	1	1.648691	-2.618316	1.636355
21	6	0.000000	0.000000	1.441776
22	8	0.000000	0.000000	2.629808
23	76	0.127857	1.205482	-0.175662
24	76	-0.127857	-1.205482	-0.175662

Table S13. Theoretical Cartesian coordinates (in Å) for the structure **OsI-Q** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.191536	-1.506789	1.031035
2	6	2.567645	-1.764521	-0.322012
3	6	3.323957	-0.636011	-0.789313
4	6	3.413496	0.319419	0.249761
5	6	2.674745	-0.191345	1.374326
6	1	1.648693	-2.173845	1.687905
7	1	2.359304	-2.664915	-0.886019
8	1	3.724860	-0.520302	-1.789651
9	1	3.902810	1.283366	0.195930
10	1	2.570135	0.293071	2.336862
11	6	-2.056006	-1.868958	0.559408
12	6	-2.950404	-0.887655	1.099317
13	6	-1.998437	-1.696535	-0.845323
14	1	-1.476685	-2.578094	1.137258
15	6	-3.495287	-0.142782	0.011944
16	1	-3.205738	-0.773940	2.145561
17	6	-2.856604	-0.594051	-1.193021
18	1	-1.391205	-2.267782	-1.534888
19	1	-4.219946	0.658688	0.086871
20	1	-3.065322	-0.247511	-2.197198
21	6	0.338833	1.792906	-0.019317
22	8	0.282459	2.975729	0.087003
23	76	-1.268919	0.327777	0.081329
24	76	1.136979	0.043846	-0.197375

Table S14. Theoretical Cartesian coordinates (in Å) for the structure **OsI-Q'** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.273783	1.199513	2.416248
2	6	-1.426857	-0.006417	3.157419
3	6	-0.135916	-0.420433	3.601346
4	6	0.833993	0.537544	3.175927
5	6	0.134239	1.540812	2.414315
6	1	-2.068317	1.772360	1.955752
7	1	-2.353744	-0.543947	3.315727
8	1	0.074897	-1.328855	4.153767
9	1	1.895888	0.521735	3.383598
10	1	0.575806	2.432221	1.986923
11	6	0.134239	1.540812	-2.414315
12	6	0.833993	0.537544	-3.175927
13	6	-1.273783	1.199513	-2.416248
14	1	0.575806	2.432221	-1.986923
15	6	-0.135916	-0.420433	-3.601346
16	1	1.895888	0.521735	-3.383598
17	6	-1.426857	-0.006417	-3.157419
18	1	-2.068317	1.772360	-1.955752
19	1	0.074897	-1.328855	-4.153767
20	1	-2.353744	-0.543947	-3.315727
21	6	1.508100	0.042102	0.000000
22	8	2.653539	0.391818	0.000000
23	76	-0.027014	-0.284910	-1.256172
24	76	-0.027014	-0.284910	1.256172

Table S15. Theoretical Cartesian coordinates (in Å) for the structure **OsI-H** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.343148	3.197536	0.356178
2	6	2.173523	2.609120	-0.654627
3	6	1.323843	2.192966	-1.732598
4	6	-0.021752	2.515152	-1.368063
5	6	0.000000	3.166683	-0.102937
6	1	1.685672	3.614717	1.295404
7	1	3.255240	2.548599	-0.633302
8	1	1.643185	1.752539	-2.668956
9	1	-0.902706	2.316980	-1.965215
10	1	-0.867916	3.496832	0.454944
11	6	0.000000	-3.166683	-0.102937
12	6	-1.343148	-3.197536	0.356178
13	6	0.021752	-2.515152	-1.368063
14	1	0.867916	-3.496832	0.454944
15	6	-2.173523	-2.609120	-0.654627
16	1	-1.685672	-3.614717	1.295404
17	6	-1.323843	-2.192966	-1.732598
18	1	0.902706	-2.316980	-1.965215
19	1	-3.255240	-2.548599	-0.633302
20	1	-1.643185	-1.752539	-2.668956
21	6	0.000000	0.000000	1.705597
22	8	0.000000	0.000000	2.894929
23	76	-0.923288	-0.859923	0.103064
24	76	0.923288	0.859923	0.103064

Table S16. Theoretical Cartesian coordinates (in Å) for the structure **OsI'-H** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.998053	0.378886	1.904512
2	6	-1.523233	-0.679208	2.736367
3	6	-0.385147	-0.192287	3.449943
4	6	-0.156154	1.167344	3.043699
5	6	-1.179702	1.520686	2.116712
6	1	-2.843210	0.316926	1.231548
7	1	-1.960852	-1.666013	2.824779
8	1	0.184229	-0.737794	4.193498
9	1	0.615755	1.825158	3.423474
10	1	-1.270260	2.473019	1.608809
11	6	-0.156154	1.167344	-3.043699
12	6	-0.385147	-0.192287	-3.449943
13	6	-1.179702	1.520686	-2.116712
14	1	0.615755	1.825158	-3.423474
15	6	-1.523233	-0.679208	-2.736367
16	1	0.184229	-0.737794	-4.193498
17	6	-1.998053	0.378886	-1.904512
18	1	-1.270260	2.473019	-1.608809
19	1	-1.960852	-1.666013	-2.824779
20	1	-2.843210	0.316926	-1.231548
21	6	1.599891	0.592635	0.000000
22	8	2.592794	1.251427	0.000000
23	76	0.283648	-0.291677	-1.267206
24	76	0.283648	-0.291677	1.267206

Table S17. Theoretical Cartesian coordinates (in Å) for the structure **ReI-S** (C_2) using the BP86/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	2.669849	-1.526173
2	6	-1.357013	2.986045	-1.130512
3	6	-1.333357	3.389417	0.248055
4	6	0.005315	3.284603	0.734617
5	6	0.847481	2.835583	-0.359047
6	1	0.335895	2.391753	-2.528269
7	1	-2.237668	2.958698	-1.777999
8	1	-2.209749	3.644427	0.851723
9	1	0.337104	3.486066	1.756195
10	1	1.934161	2.733251	-0.334115
11	75	-0.465247	1.042767	-0.033956
12	75	0.465247	-1.042767	-0.033956
13	6	-0.847481	-2.835583	-0.359047
14	6	0.000000	-2.669849	-1.526173
15	6	-0.005315	-3.284603	0.734617
16	1	-1.934161	-2.733251	-0.334115
17	6	1.357013	-2.986045	-1.130512
18	1	-0.335895	-2.391753	-2.528269
19	6	1.333357	-3.389417	0.248055
20	1	-0.337104	-3.486066	1.756195
21	1	2.237668	-2.958698	-1.777999
22	1	2.209749	-3.644427	0.851723
23	6	0.000000	0.000000	1.703724
24	8	0.000000	0.000000	2.916595

Table S18. Theoretical Cartesian coordinates (in Å) for the structure **ReI-S** (C_1) using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.369791	-1.604674	0.471949
2	6	3.243667	-1.096318	-0.559749
3	6	3.627329	0.210804	-0.196979
4	6	2.990553	0.575186	1.023227
5	6	2.241259	-0.574086	1.471732
6	1	1.983857	-2.613448	0.539844
7	1	3.547920	-1.625677	-1.454256
8	1	4.220383	0.880639	-0.811492
9	1	3.116235	1.508265	1.556781
10	1	1.732472	-0.665412	2.421553
11	75	1.177589	0.049371	-0.309210
12	75	-1.081753	-0.021214	0.175967
13	6	-2.848966	0.083614	-1.223163
14	6	-2.471598	-1.288682	-1.025581
15	6	-3.400068	0.569184	0.007569
16	1	-2.794410	0.630070	-2.155593
17	6	-2.746478	-1.619839	0.342599
18	1	-2.083104	-1.953649	-1.785588
19	6	-3.321102	-0.469179	0.966180
20	1	-3.756462	1.575986	0.187231
21	1	-2.586189	-2.582485	0.812691
22	1	-3.609723	-0.392213	2.007913
23	6	-0.421938	1.784947	0.101544
24	8	-0.316671	2.962544	0.049778

Table S19. Theoretical Cartesian coordinates (in Å) for the structure **ReI-T** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.635693	-0.260659	-1.357067
2	6	-2.054896	-1.524302	-0.982225
3	6	-2.453340	-1.804961	0.359492
4	6	-3.331294	-0.754894	0.786418
5	6	-3.455188	0.181381	-0.262694
6	1	-2.570820	0.210246	-2.329471
7	1	-1.449933	-2.160664	-1.614457
8	1	-2.181781	-2.681830	0.933947
9	1	-3.790216	-0.674060	1.765042
10	1	-4.023241	1.103036	-0.233439
11	75	-1.123671	0.121197	0.260761
12	75	1.173435	-0.072666	-0.323797
13	6	2.259310	-0.219667	1.488556
14	6	2.513677	-1.444565	0.747009
15	6	2.886291	0.871758	0.759462
16	1	1.784229	-0.148352	2.457956
17	6	3.365000	-1.093273	-0.356149
18	1	2.258634	-2.449190	1.058211
19	6	3.594603	0.296063	-0.339541
20	1	2.919640	1.910996	1.061856
21	1	3.710573	-1.780297	-1.120514
22	1	4.130100	0.856348	-1.097895
23	6	-0.697342	1.963227	0.023847
24	8	-0.558278	3.114169	-0.169524

Table S20. Theoretical Cartesian coordinates (in Å) for the structure **ReI-Q** (C_{2v}) using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.174561	3.098544	0.438631
2	6	0.718313	3.390878	-0.901138
3	6	-0.718313	3.390878	-0.901138
4	6	-1.174561	3.098544	0.438631
5	6	0.000000	2.922684	1.273153
6	1	2.213969	3.047360	0.771789
7	1	1.356808	3.548081	-1.775115
8	1	-1.356808	3.548081	-1.775115
9	1	-2.213969	3.047360	0.771789
10	1	0.000000	2.697743	2.342780
11	75	0.000000	1.248450	-0.227333
12	75	0.000000	-1.248450	-0.227333
13	6	0.000000	-2.922684	1.273153
14	6	-1.174561	-3.098544	0.438631
15	6	1.174561	-3.098544	0.438631
16	1	0.000000	-2.697743	2.342780
17	6	-0.718313	-3.390878	-0.901138
18	1	-2.213969	-3.047360	0.771789
19	6	0.718313	-3.390878	-0.901138
20	1	2.213969	-3.047360	0.771789
21	1	-1.356808	-3.548081	-1.775115
22	1	1.356808	-3.548081	-1.775115
23	6	0.000000	0.000000	1.392138
24	8	0.000000	0.000000	2.612003

Table S21. Theoretical Cartesian coordinates (in Å) for the structure **ReI-Q** (C_2) using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.927711	3.313684	0.317273
2	6	0.324363	3.454013	-0.964874
3	6	-1.068766	3.179819	-0.836098
4	6	-1.341276	2.848359	0.536630
5	6	-0.088290	2.930954	1.248917
6	1	1.980601	3.438563	0.539858
7	1	0.839631	3.700916	-1.885495
8	1	-1.793539	3.202134	-1.641457
9	1	-2.311462	2.653576	0.974980
10	1	0.048639	2.745258	2.307115
11	75	0.000000	1.253045	-0.221674
12	75	0.000000	-1.253045	-0.221674
13	6	0.088290	-2.930954	1.248917
14	6	-0.927711	-3.313684	0.317273
15	6	1.341276	-2.848359	0.536630
16	1	-0.048639	-2.745258	2.307115
17	6	-0.324363	-3.454013	-0.964874
18	1	-1.980601	-3.438563	0.539858
19	6	1.068766	-3.179819	-0.836098
20	1	2.311462	-2.653576	0.974980
21	1	-0.839631	-3.700916	-1.885495
22	1	1.793539	-3.202134	-1.641457
23	6	0.000000	0.000000	1.388991
24	8	0.000000	0.000000	2.588118

Table S22. Theoretical Cartesian coordinates (in Å) for the structure **ReI-H** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.062417	-1.969208	0.156231
2	6	3.012650	-1.332676	-0.698528
3	6	3.581024	-0.225107	-0.001611
4	6	2.944061	-0.121505	1.264648
5	6	1.993188	-1.198482	1.361379
6	1	1.496218	-2.863115	-0.070693
7	1	3.280146	-1.654052	-1.698180
8	1	4.325731	0.456873	-0.394572
9	1	3.155320	0.612832	2.031437
10	1	1.383955	-1.420074	2.228182
11	75	1.246763	0.171721	-0.265258
12	75	-1.265079	0.318966	-0.123791
13	6	-2.597772	-0.869915	1.418266
14	6	-3.486582	-0.145312	0.568897
15	6	-1.958763	-1.888470	0.637531
16	1	-2.474579	-0.718414	2.484369
17	6	-3.333187	-0.663768	-0.748803
18	1	-4.137672	0.667563	0.866413
19	6	-2.407909	-1.757921	-0.695932
20	1	-1.238783	-2.610109	1.000856
21	1	-3.864127	-0.324661	-1.630738
22	1	-2.086466	-2.358576	-1.538163
23	6	0.300109	1.814589	0.255822
24	8	0.109813	2.944614	0.599046

Table S23. Theoretical Cartesian coordinates (in Å) for the structure **WI-S** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.762317	-1.667796	0.795321
2	6	2.640391	-1.660409	-0.342754
3	6	3.554292	-0.575619	-0.150987
4	6	3.252244	0.089102	1.049758
5	6	2.112321	-0.552662	1.637167
6	1	1.014120	-2.420054	1.008025
7	1	2.680001	-2.404274	-1.127532
8	1	4.327258	-0.278807	-0.853211
9	1	3.749778	0.970366	1.436151
10	1	1.691817	-0.316872	2.607032
11	6	-2.366047	0.515361	1.429905
12	6	-3.501858	0.121193	0.656051
13	6	-1.506669	-0.652966	1.516255
14	1	-2.263265	1.430197	2.000255
15	6	-3.326092	-1.191573	0.199535
16	1	-4.322814	0.774814	0.377276
17	6	-2.067943	-1.699613	0.671916
18	1	-0.678726	-0.764774	2.201507
19	1	-3.992655	-1.713189	-0.480108
20	1	-1.744798	-2.731624	0.619117
21	6	0.470546	1.910405	0.303634
22	8	0.187871	2.953545	0.787031
23	74	-1.248175	0.034145	-0.503214
24	74	1.138653	0.182252	-0.316780

Table S24. Theoretical Cartesian coordinates (in Å) for the structure **WI-T_1** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.299097	0.446230	-1.115507
2	6	2.941530	1.576133	-0.321615
3	6	2.866584	1.155485	1.044244
4	6	3.186527	-0.245327	1.086733
5	6	3.468906	-0.667484	-0.250210
6	1	3.421061	0.438465	-2.192054
7	1	2.761434	2.578503	-0.693328
8	1	2.665867	1.787300	1.901068
9	1	3.259537	-0.856026	1.977529
10	1	3.724627	-1.674050	-0.556803
11	6	-3.597601	0.379308	0.029104
12	6	-2.922939	0.916587	1.160692
13	6	-2.945037	0.891576	-1.131158
14	1	-4.420105	-0.324534	0.045960
15	6	-1.896463	1.804287	0.707326
16	1	-3.149192	0.695395	2.197783
17	6	-1.912943	1.792962	-0.718892
18	1	-3.198791	0.653980	-2.158139
19	1	-1.250463	2.402829	1.335057
20	1	-1.285366	2.384006	-1.371672
21	6	0.271348	-1.666886	-0.013053
22	8	-0.786724	-2.394678	0.052442
23	74	1.172227	-0.006634	-0.051531
24	74	-1.345050	-0.361281	0.000573

Table S25. Theoretical Cartesian coordinates (in Å) for the structure **WI-T_2** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.840636	-0.684510	-1.295095
2	6	-2.780630	-1.641217	-0.234894
3	6	-3.215611	-1.003091	0.961339
4	6	-3.552966	0.344141	0.644855
5	6	-3.321344	0.542639	-0.741810
6	1	-2.601538	-0.868487	-2.334464
7	1	-2.468405	-2.673962	-0.331770
8	1	-3.279670	-1.462663	1.940480
9	1	-3.898591	1.095533	1.344883
10	1	-3.470253	1.467839	-1.286045
11	6	2.344406	-0.289448	1.579617
12	6	1.947062	-1.545565	1.013576
13	6	3.355331	0.273707	0.743946
14	1	1.970399	0.137083	2.501041
15	6	2.724617	-1.754463	-0.171975
16	1	1.252087	-2.246738	1.455011
17	6	3.572229	-0.626002	-0.334603
18	1	3.853340	1.223076	0.895696
19	1	2.678959	-2.618922	-0.822900
20	1	4.254051	-0.462472	-1.162370
21	6	0.525768	1.869549	0.067622
22	8	0.243873	2.980485	0.381917
23	74	-1.151184	0.015642	0.157707
24	74	1.248606	0.114782	-0.409739

Table S26. Theoretical Cartesian coordinates (in Å) for the structure **WI-Q** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.485109	0.300569	-0.697518
2	6	-3.298800	-1.109230	-0.603241
3	6	-2.949310	-1.417719	0.745117
4	6	-2.920765	-0.196074	1.483771
5	6	-3.247015	0.864353	0.588455
6	1	-3.752344	0.849804	-1.592524
7	1	-3.410572	-1.823233	-1.410566
8	1	-2.760072	-2.407988	1.142438
9	1	-2.702517	-0.091973	2.539980
10	1	-3.290459	1.917465	0.840662
11	6	2.200282	-0.200512	1.649980
12	6	1.851366	-1.479677	1.097069
13	6	3.291817	0.326826	0.887905
14	1	1.751308	0.259297	2.520486
15	6	2.747422	-1.740511	0.006258
16	1	1.127956	-2.171474	1.505325
17	6	3.610505	-0.625519	-0.122243
18	1	3.785759	1.275788	1.053923
19	1	2.751574	-2.625787	-0.618169
20	1	4.368641	-0.500157	-0.888180
21	6	0.474943	1.801589	0.140130
22	8	0.083892	2.835893	0.580771
23	74	1.326344	0.149101	-0.410557
24	74	-1.166782	-0.101986	-0.140709

Table S27. Theoretical Cartesian coordinates (in Å) for the structure **WI-H** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	1.064825	3.224258	1.153875
2	6	1.900440	3.157259	0.000000
3	6	1.064825	3.224258	-1.153875
4	6	-0.289723	3.338806	-0.718501
5	6	-0.289723	3.338806	0.718501
6	1	1.400089	3.195057	2.183973
7	1	2.979883	3.060301	0.000000
8	1	1.400089	3.195057	-2.183973
9	1	-1.161479	3.435823	-1.352795
10	1	-1.161479	3.435823	1.352795
11	6	-1.583934	-3.020699	-0.714818
12	6	-0.289723	-3.424186	-1.154685
13	6	-1.583934	-3.020699	0.714818
14	1	-2.422359	-2.754307	-1.347329
15	6	0.511341	-3.666054	0.000000
16	1	0.030487	-3.525139	-2.184872
17	6	-0.289723	-3.424186	1.154685
18	1	-2.422359	-2.754307	1.347329
19	1	1.548066	-3.981252	0.000000
20	1	0.030487	-3.525139	2.184872
21	6	-1.371100	0.605071	0.000000
22	8	-2.567434	0.505846	0.000000
23	74	0.451739	1.263178	0.000000
24	74	-0.083407	-1.341888	0.000000

Table S28. Theoretical Cartesian coordinates (in Å) for the structure **TaI-S$_1$** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.352530	1.282871	-1.301032
2	6	-3.412693	0.442314	-0.832820
3	6	-3.544563	0.618248	0.560648
4	6	-2.564816	1.565010	0.979675
5	6	-1.859669	2.009930	-0.175287
6	1	-2.054154	1.418606	-2.331566
7	1	-3.993110	-0.241331	-1.443417
8	1	-4.237132	0.092966	1.208789
9	1	-2.427966	1.924469	1.993473
10	1	-1.082931	2.763285	-0.200087
11	6	2.535318	0.587699	1.510430
12	6	3.551204	0.198415	0.586013
13	6	1.777892	1.641510	0.906190
14	1	2.392700	0.190062	2.506977
15	6	3.434685	1.022062	-0.569311
16	1	4.295103	-0.574284	0.744556
17	6	2.351750	1.908581	-0.377971
18	1	0.994661	2.212424	1.385831
19	1	4.058153	0.963516	-1.455366
20	1	2.012344	2.656622	-1.085429
21	6	0.178198	-1.860984	0.206739
22	8	-1.043795	-2.318316	0.345027
23	73	-1.227061	-0.305907	0.115877
24	73	1.334240	-0.370171	-0.294557

Table S29. Theoretical Cartesian coordinates (in Å) for the structure **TaI-S_2** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.927977	0.259357	2.198510
2	6	-1.230597	-0.297187	3.296788
3	6	-0.047046	0.464696	3.497363
4	6	-0.014061	1.532109	2.545291
5	6	-1.191710	1.397222	1.745524
6	1	-2.864199	-0.098852	1.790274
7	1	-1.522442	-1.183703	3.849568
8	1	0.710726	0.269653	4.249842
9	1	0.720415	2.325035	2.484771
10	1	-1.502245	2.084462	0.972973
11	6	-0.014061	1.532109	-2.545291
12	6	-0.047046	0.464696	-3.497363
13	6	-1.191710	1.397222	-1.745524
14	1	0.720415	2.325035	-2.484771
15	6	-1.230597	-0.297187	-3.296788
16	1	0.710726	0.269653	-4.249842
17	6	-1.927977	0.259357	-2.198510
18	1	-1.502245	2.084462	-0.972973
19	1	-1.522442	-1.183703	-3.849568
20	1	-2.864199	-0.098852	-1.790274
21	6	1.530122	0.676500	0.000000
22	8	2.481264	1.426754	0.000000
23	73	0.224804	-0.428360	1.283573
24	73	0.224804	-0.428360	-1.283573

Table S30. Theoretical Cartesian coordinates (in Å) for the structure **TaI-T** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-2.484792	0.435382	1.580449
2	6	-1.735552	1.537619	1.057962
3	6	-2.347761	1.936469	-0.171239
4	6	-3.458541	1.086647	-0.403576
5	6	-3.547137	0.161396	0.667944
6	1	-2.304212	-0.069582	2.520963
7	1	-0.915273	2.038957	1.552935
8	1	-2.027676	2.752993	-0.807716
9	1	-4.115196	1.122271	-1.266608
10	1	-4.290601	-0.620649	0.774751
11	6	2.698661	1.048884	-1.319029
12	6	1.917642	1.936671	-0.525751
13	6	3.601810	0.360846	-0.452287
14	1	2.655252	0.955570	-2.397624
15	6	2.288393	1.742957	0.835551
16	1	1.169282	2.625614	-0.894975
17	6	3.347397	0.782689	0.870162
18	1	4.329374	-0.383862	-0.755961
19	1	1.895222	2.282865	1.688853
20	1	3.848989	0.423125	1.761954
21	6	-0.226470	-1.819851	0.194849
22	8	0.951205	-2.288735	0.543593
23	73	-1.362310	-0.332893	-0.358121
24	73	1.250300	-0.325678	0.076813

Table S31. Theoretical Cartesian coordinates (in Å) for the structure **TaI-Q** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	3.138882	0.001598
2	6	-0.001461	2.614074	-1.329366
3	6	-1.363892	2.489080	-1.743111
4	6	-2.187816	2.908633	-0.668644
5	6	-1.350155	3.328210	0.404055
6	1	0.878468	3.369354	0.591337
7	1	0.872046	2.416101	-1.935436
8	1	-1.708177	2.124626	-2.703910
9	1	-3.272450	2.911204	-0.664227
10	1	-1.683534	3.704564	1.364225
11	6	1.350155	-3.328210	0.404055
12	6	0.000000	-3.138882	0.001598
13	6	2.187816	-2.908633	-0.668644
14	1	1.683534	-3.704564	1.364225
15	6	0.001461	-2.614074	-1.329366
16	1	-0.878468	-3.369354	0.591337
17	6	1.363892	-2.489080	-1.743111
18	1	3.272450	-2.911204	-0.664227
19	1	-0.872046	-2.416101	-1.935436
20	1	1.708177	-2.124626	-2.703910
21	6	0.000000	0.000000	1.843522
22	8	0.000000	0.000000	3.041328
23	73	0.909108	-0.926783	0.077602
24	73	-0.909108	0.926783	0.077602

Table S32. Theoretical Cartesian coordinates (in Å) for the structure **TaI-H** (C_2) using the BP86/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.427343	3.579196	-0.912519
2	6	-0.979787	3.669575	-0.709182
3	6	-1.242569	3.390780	0.669324
4	6	0.000000	3.130847	1.313946
5	6	1.034168	3.249890	0.336071
6	1	0.946453	3.733916	-1.851052
7	1	-1.716194	3.918272	-1.464452
8	1	-2.215551	3.381799	1.146935
9	1	0.132889	2.867763	2.356542
10	1	2.094410	3.114162	0.513443
11	6	-1.034168	-3.249890	0.336071
12	6	-0.427343	-3.579196	-0.912519
13	6	0.000000	-3.130847	1.313946
14	1	-2.094410	-3.114162	0.513443
15	6	0.979787	-3.669575	-0.709182
16	1	-0.946453	-3.733916	-1.851052
17	6	1.242569	-3.390780	0.669324
18	1	-0.132889	-2.867763	2.356542
19	1	1.716194	-3.918272	-1.464452
20	1	2.215551	-3.381799	1.146935
21	6	0.000000	0.000000	1.398514
22	8	0.000000	0.000000	2.610081
23	73	-0.322828	1.402095	-0.267440
24	73	0.322828	-1.402095	-0.267440

Table S33. Theoretical Cartesian coordinates (in Å) for the structure **TaI-H** (C_1) using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.423715	-1.294058	-0.507285
2	6	-3.421677	-1.111484	0.900241
3	6	-3.457984	0.291151	1.168104
4	6	-3.486708	0.977940	-0.082586
5	6	-3.448363	-0.003568	-1.119754
6	1	-3.400310	-2.244475	-1.027991
7	1	-3.401124	-1.899590	1.644691
8	1	-3.486745	0.752989	2.147882
9	1	-3.541071	2.050686	-0.220113
10	1	-3.477473	0.195158	-2.184560
11	6	2.866882	0.592248	1.384325
12	6	2.900546	-0.836893	1.412797
13	6	3.491851	1.024825	0.174381
14	1	2.454247	1.236467	2.151558
15	6	3.548719	-1.286586	0.222497
16	1	2.522222	-1.465781	2.209756
17	6	3.905575	-0.140783	-0.535657
18	1	3.641278	2.053410	-0.131301
19	1	3.733222	-2.317975	-0.052566
20	1	4.395759	-0.152218	-1.503280
21	6	-0.397678	1.667089	-0.005715
22	8	-0.053153	2.806156	0.001535
23	73	-1.370655	-0.115582	0.040572
24	73	1.459977	-0.157530	-0.329810

Table S34. Theoretical Cartesian coordinates (in Å) for the structure **OsII-T** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.046695	0.269038	0.000000
2	6	1.898691	1.102968	1.163828
3	6	1.676470	2.446660	0.718567
4	6	1.676470	2.446660	-0.718567
5	6	1.898691	1.102968	-1.163828
6	1	2.344554	-0.778389	0.000000
7	1	1.971663	0.771870	2.191529
8	1	1.538950	3.311652	1.355121
9	1	1.538950	3.311652	-1.355121
10	1	1.971663	0.771870	-2.191529
11	6	-1.821236	2.166867	-0.718646
12	6	-1.821236	2.166867	0.718646
13	6	-1.821236	0.808285	-1.165449
14	1	-1.827248	3.044516	-1.353084
15	6	-1.821236	0.808285	1.165449
16	1	-1.827248	3.044516	1.353084
17	6	-1.816979	-0.047336	0.000000
18	1	-1.842565	0.468097	-2.192556
19	1	-1.842565	0.468097	2.192556
20	1	-2.041592	-1.139964	0.000000
21	6	-0.100169	-3.499412	0.000000
22	8	-0.183612	-4.673158	0.000000
23	76	0.019678	1.215227	0.000000
24	76	0.000254	-1.669434	0.000000

Table S35. Theoretical Cartesian coordinates (in Å) for the structure **ReII-T** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.906525	-1.824322	1.178536
2	6	2.259313	-1.777156	0.721135
3	6	2.261332	-1.777387	-0.716686
4	6	0.909849	-1.824518	-1.177869
5	6	0.049550	-1.817898	-0.000872
6	1	0.568116	-1.888885	2.204409
7	1	3.139550	-1.766196	1.352183
8	1	3.143354	-1.766576	-1.345242
9	1	0.574271	-1.889179	-2.204664
10	1	-1.070866	-2.126642	-0.002129
11	6	0.647072	1.888351	-1.180600
12	6	1.994765	2.007006	-0.719745
13	6	-0.190828	1.770756	-0.000745
14	1	0.298107	1.919316	-2.204175
15	6	1.993700	2.007468	0.721240
16	1	2.868737	2.111982	-1.350617
17	6	0.645389	1.889037	1.180187
18	1	-1.347634	1.876043	-0.001276
19	1	2.866761	2.112696	1.353330
20	1	0.294899	1.920354	2.203228
21	75	-1.470548	-0.129200	-0.001774
22	75	1.156632	0.047962	0.000484
23	6	-3.384662	0.065959	0.002488
24	8	-4.542949	0.243271	0.006163

Table S36. Theoretical Cartesian coordinates (in Å) for the structure **ReII-Q** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.720580	2.056286	-0.393307
2	6	-1.167475	1.793486	-1.727521
3	6	0.000000	1.657379	-2.550608
4	6	1.167475	1.793486	-1.727521
5	6	0.720580	2.056286	-0.393307
6	1	-1.359671	2.315431	0.444364
7	1	-2.196738	1.775650	-2.061666
8	1	0.000000	1.463445	-3.616241
9	1	2.196738	1.775650	-2.061666
10	1	1.359671	2.315431	0.444364
11	6	1.167475	-1.793486	-1.727521
12	6	0.000000	-1.657379	-2.550608
13	6	0.720580	-2.056286	-0.393307
14	1	2.196738	-1.775650	-2.061666
15	6	-1.167475	-1.793486	-1.727521
16	1	0.000000	-1.463445	-3.616241
17	6	-0.720580	-2.056286	-0.393307
18	1	1.359671	-2.315431	0.444364
19	1	-2.196738	-1.775650	-2.061666
20	1	-1.359671	-2.315431	0.444364
21	75	0.000000	0.000000	1.580299
22	75	0.000000	0.000000	-1.092325
23	6	0.000000	0.000000	3.516303
24	8	0.000000	0.000000	4.689123

Table S37. Theoretical Cartesian coordinates (in Å) for the structure **ReII-H** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.004926	-0.002133	0.721602
2	6	1.996804	1.357407	1.168019
3	6	2.021097	2.189423	0.000000
4	6	1.996804	1.357407	-1.168019
5	6	2.004926	-0.002133	-0.721602
6	1	2.108712	-0.872580	1.359649
7	1	2.042575	1.690332	2.196737
8	1	2.028671	3.272618	0.000000
9	1	2.042575	1.690332	-2.196737
10	1	2.108712	-0.872580	-1.359649
11	6	-1.485266	2.095079	-1.168184
12	6	-1.166915	2.865419	0.000000
13	6	-2.039599	0.854158	-0.721834
14	1	-1.388735	2.416493	-2.197153
15	6	-1.485266	2.095079	1.168184
16	1	-0.732382	3.857886	0.000000
17	6	-2.039599	0.854158	0.721834
18	1	-2.478492	0.095517	-1.359886
19	1	-1.388735	2.416493	2.197153
20	1	-2.478492	0.095517	1.359886
21	75	-0.406806	-1.578179	0.000000
22	75	0.112778	1.066060	0.000000
23	6	0.743323	-3.430267	0.000000
24	8	0.610031	-4.597836	0.000000

Table S38. Theoretical Cartesian coordinates (in Å) for the structure **WII-T** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-0.699214	0.372276	2.194357
2	6	-1.147085	1.667796	1.767993
3	6	0.032300	2.460279	1.565512
4	6	1.194283	1.646620	1.800393
5	6	0.727919	0.373880	2.224548
6	1	-1.337101	-0.442465	2.518875
7	1	-2.172583	2.011564	1.740616
8	1	0.045786	3.500015	1.263675
9	1	2.228214	1.962166	1.754926
10	1	1.353033	-0.472154	2.481068
11	6	1.194283	1.646620	-1.800393
12	6	0.032300	2.460279	-1.565512
13	6	0.727919	0.373880	-2.224548
14	1	2.228214	1.962166	-1.754926
15	6	-1.147085	1.667796	-1.767993
16	1	0.045786	3.500015	-1.263675
17	6	-0.699214	0.372276	-2.194357
18	1	1.353033	-0.472154	-2.481068
19	1	-2.172583	2.011564	-1.740616
20	1	-1.337101	-0.442465	-2.518875
21	6	1.474148	-1.776021	0.000000
22	8	2.653934	-1.910331	0.000000
23	74	0.003668	0.812147	0.000000
24	74	-0.430824	-1.696332	0.000000

Table S39. Theoretical Cartesian coordinates (in Å) for the structure **WII-Q** (C_s) using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.783659	-0.556058	2.167803
2	6	0.940441	-1.924983	1.778528
3	6	-0.377830	-2.465370	1.605339
4	6	-1.348495	-1.425665	1.815248
5	6	-0.617545	-0.257331	2.191205
6	1	1.583742	0.103743	2.481599
7	1	1.874852	-2.468820	1.734954
8	1	-0.605430	-3.488467	1.331932
9	1	-2.424971	-1.532406	1.816295
10	1	-1.060056	0.689568	2.478329
11	6	-1.348495	-1.425665	-1.815248
12	6	-0.377830	-2.465370	-1.605339
13	6	-0.617545	-0.257331	-2.191205
14	1	-2.424971	-1.532406	-1.816295
15	6	0.940441	-1.924983	-1.778528
16	1	-0.605430	-3.488467	-1.331932
17	6	0.783659	-0.556058	-2.167803
18	1	-1.060056	0.689568	-2.478329
19	1	1.874852	-2.468820	-1.734954
20	1	1.583742	0.103743	-2.481599
21	6	-1.175308	2.691940	0.000000
22	8	-2.236550	3.170948	0.000000
23	74	-0.062501	-0.901168	0.000000
24	74	0.517166	1.596120	0.000000

Table S40. Theoretical Cartesian coordinates (in Å) for the structure **WII-Q** (C_1) using the BP86/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.483777	2.043729	-1.140657
2	6	1.891535	1.736085	-1.217006
3	6	2.432733	1.821701	0.118911
4	6	1.357079	2.122902	1.036932
5	6	0.159526	2.285965	0.246466
6	1	-0.200582	2.135941	-1.987437
7	1	2.454629	1.531330	-2.130801
8	1	3.474053	1.637760	0.397882
9	1	1.444999	2.285403	2.113466
10	1	-0.820827	2.573983	0.632960
11	6	1.721211	-1.594817	1.519639
12	6	2.543500	-1.575491	0.331866
13	6	0.395788	-1.991401	1.139033
14	1	2.054801	-1.385706	2.539097
15	6	1.721228	-1.885532	-0.815633
16	1	3.604937	-1.313853	0.301723
17	6	0.372294	-2.150802	-0.315756
18	1	-0.441056	-2.162134	1.820902
19	1	2.058974	-2.026462	-1.844492
20	1	-0.420413	-2.654598	-0.889805
21	6	-2.793664	0.603854	0.860359
22	8	-3.405227	1.191029	1.700502
23	74	0.927654	0.057049	0.067221
24	74	-1.571948	-0.309037	-0.406984

Table S41. Theoretical Cartesian coordinates (in Å) for the structure **TaII-T** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.369368	0.516773	0.709130
2	6	1.954111	1.805691	1.157575
3	6	1.714759	2.607001	0.000000
4	6	1.954111	1.805691	-1.157575
5	6	2.369368	0.516773	-0.709130
6	1	2.630616	-0.320006	1.342972
7	1	1.878728	2.132123	2.187695
8	1	1.402567	3.644947	0.000000
9	1	1.878728	2.132123	-2.187695
10	1	2.630616	-0.320006	-1.342972
11	6	-1.818840	1.626378	-1.157665
12	6	-1.692555	2.446757	0.000000
13	6	-2.133277	0.284318	-0.724404
14	1	-1.780165	1.954778	-2.188450
15	6	-1.818840	1.626378	1.157665
16	1	-1.499413	3.513010	0.000000
17	6	-2.133277	0.284318	0.724404
18	1	-2.541628	-0.476542	-1.384761
19	1	-1.780165	1.954778	2.188450
20	1	-2.541628	-0.476542	1.384761
21	6	1.238646	-2.689244	0.000000
22	8	2.298355	-3.193391	0.000000
23	73	0.065266	0.870533	0.000000
24	73	-0.485630	-1.598979	0.000000

Table S42. Theoretical Cartesian coordinates (in Å) for the structure **TaII-Q** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.327335	0.520261	0.714321
2	6	1.973580	1.825847	1.155719
3	6	1.756547	2.632563	0.000000
4	6	1.973580	1.825847	-1.155719
5	6	2.327335	0.520261	-0.714321
6	1	2.579929	-0.319340	1.348384
7	1	1.902941	2.154137	2.185827
8	1	1.471145	3.678549	0.000000
9	1	1.902941	2.154137	-2.185827
10	1	2.579929	-0.319340	-1.348384
11	6	-1.880234	1.585041	-1.156999
12	6	-1.831712	2.405409	0.000000
13	6	-2.064657	0.211113	-0.730392
14	1	-1.887644	1.923685	-2.185519
15	6	-1.880234	1.585041	1.156999
16	1	-1.696202	3.481306	0.000000
17	6	-2.064657	0.211113	0.730392
18	1	-2.456868	-0.566745	-1.386659
19	1	-1.887644	1.923685	2.185519
20	1	-2.456868	-0.566745	1.386659
21	6	1.298557	-2.692578	0.000000
22	8	2.385433	-3.129672	0.000000
23	73	0.053829	0.937652	0.000000
24	73	-0.475032	-1.653891	0.000000

Table S43. Theoretical Cartesian coordinates (in Å) for the structure **TaII-H** using the MPW1PW91/SDD method

Standard orientation:

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.853116	-0.843132	2.270287
2	6	0.769516	-2.223939	1.944331
3	6	-0.607233	-2.546069	1.741046
4	6	-1.372601	-1.354895	1.934783
5	6	-0.467056	-0.298630	2.255144
6	1	1.758628	-0.297495	2.507897
7	1	1.602005	-2.914912	1.883508
8	1	-1.003097	-3.529205	1.516544
9	1	-2.451247	-1.270803	1.880676
10	1	-0.739278	0.714322	2.532850
11	6	-1.372601	-1.354895	-1.934783
12	6	-0.607233	-2.546069	-1.741046
13	6	-0.467056	-0.298630	-2.255144
14	1	-2.451247	-1.270803	-1.880676
15	6	0.769516	-2.223939	-1.944331
16	1	-1.003097	-3.529205	-1.516544
17	6	0.853116	-0.843132	-2.270287
18	1	-0.739278	0.714322	-2.532850
19	1	1.602005	-2.914912	-1.883508
20	1	1.758628	-0.297495	-2.507897
21	6	-0.996479	3.210771	0.000000
22	8	-1.929332	3.919327	0.000000
23	73	-0.031207	-1.058844	0.000000
24	73	0.482860	1.759898	0.000000

Complete Gaussian 03 reference (Reference 48)

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