Homoleptic Tetranuclear Osmium Carbonyls: From the Rhombus via the Butterfly to the Tetrahedron

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Supporting Information

Figures S1 to S7 and Tables S1 to S18: Optimized structures, total energies, relative energies, imaginary vibrational frequencies, and □(CO) frequencies for $Os_4(CO)_{16}$ (8 isomers), $Os_4(CO)_{15}$ (5 isomers), $Os_4(CO)_{14}$ (12 isomers), $Os_4(CO)_{13}$ (7 isomers), and $Os_4(CO)_{12}$ (5 isomers)

Complete Gaussian 03 reference (Reference 33)

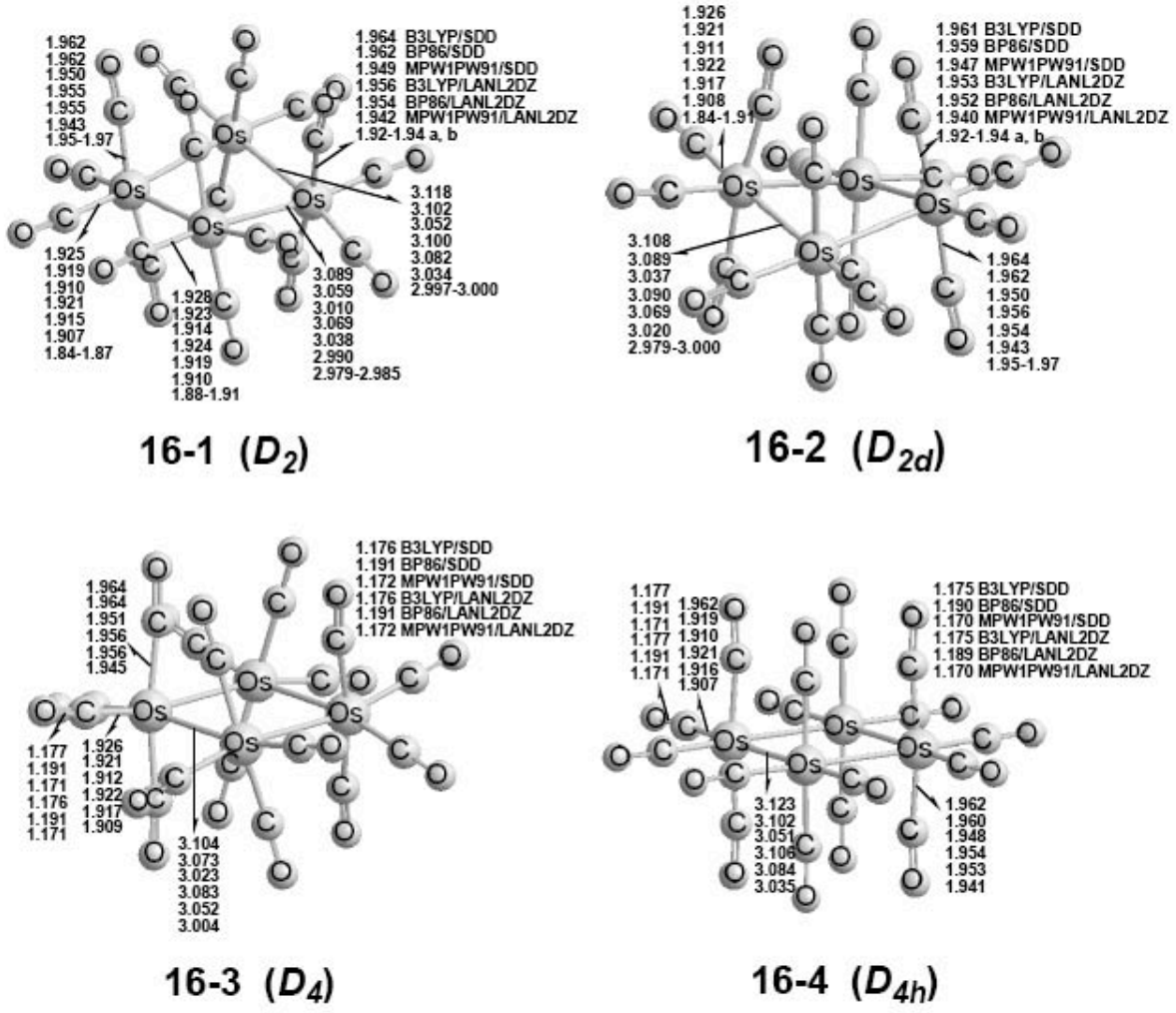


Figure S1. The four optimized structures of $Os_4(CO)_{16}$ without bridging carbonyl groups.

Table S1. The total energies (E, in Hartree) and relative energies (ΔE, in kcal/mol) of the four optimized structures of $Os_4(CO)_{16}$ without bridging carbonyl groups. The number of imaginary vibrational frequencies (Nimg) for each structure is also listed.

		16-1 (D_2)	**16-2** (D_{2d})	**16-3** (D_4)	**16-4** (D_{4h})
B3LYP/SDD	E	-2176.34426	-2176.34402	-2176.34170	-2176.33889
	ΔE	0	0.2	1.6	3.4
	Nimag	0	0	1(17i)	2(20i, 19i)
BP86/SDD	E	-2177.01905	-2177.01806	-2177.01790	-2177.01285
	ΔE	0	0.6	0.7	3.9
	Nimag	0	0	1(11i)	2(25i, 22i)
MPW1PW91/ SDD	E	-2175.90635	-2175.90502	-2175.90459	-2175.89838
	ΔE	0	0.8	1.1	5.0
	Nimag	0	1(14i)	1(16i)	2(27i, 27i)
B3LYP/ LANL2DZ	E	-2177.64112	-2177.64060	-2177.63890	-2177.63528
	ΔE	0	0.3	1.4	3.7
	Nimag	0	0	1(14i)	2(25i, 18i)
BP86/ LANL2DZ	E	-2178.21383	-2178.21226	-2178.21316	-2178.20683
	ΔE	0	1.0	0.4	4.4
	Nimag	0	1(10i)	1(8i)	2(30i, 20i)
MPW1PW91/ LANL2DZ	E	-2177.24427	-2177.242391	-2177.243032	-2177.23544
	ΔE	0	1.2	0.8	5.5
	Nimag	0	1(18i)	1(13i)	2(33i, 26i)

Table S2. The infrared □(CO) vibrational frequencies (cm^{-1}) predicted for $Os_4(CO)_{16}$ (infrared intensities in parentheses are in km/mol).

	16-1 (D_2)	**16-2** (D_{2d})
B3LYP /SDD	1930(0), 1932(7), 1941(3), 1941(6), 1948(275), 1949(251), 1950(210), 1962(396), 1969(434), 1971(0), 1985(1016), 1984(0), 2001(2054) 2024(2562), 2024(2431), 2075 (0)	1932(0), 1932(0), 1942(3), 1942(3), 1948(266), 1948(266), 1950(252), 1966(443), 1966(443), 1971(0), 1986(918), 1995(0), 2003(2102) 2024(2470), 2024(2470), 2077 (0)
BP86/SDD	1855(0), 1865(9), 1866(6), 1869(8), 1878(216), 1880(125), 1880(299), 1890(349), 1899(369), 1900(0), 1910(1845), 1918(0), 1926(701) 1949(1897), 1950(2072), 1993 (0)	1859(0), 1865(0), 1870(11), 1870(11), 1878(242), 1878(242), 1880(201), 1896(422), 1896(422), 1899(0), 1912(1477), 1921(0), 1930(972) 1951(1932), 1951(1932), 1995 (0)
MPW1PW91/ SDD	1966(0), 1974(12), 1977(8), 1980(3), 1989(293), 1990(157), 1991(362), 2000(314), 2011(369), 2013(0), 2025(1631), 2034(0), 2038(1596) 2066(2478), 2066(2714), 2118 (0)	1970(0), 1973(0), 1981(1), 1981(1), 1989(312), 1989(312), 1990(265), 2007(445), 2007(445), 2013(0), 2027(1127), 2037(0), 2045(1979) 2067(2512), 2067(2512), 2120 (0)
B3LYP/ LANL2DZ	1935(0), 1937(10), 1946(2), 1947(10), 1954(304), 1955(271), 1955(202), 1967(401), 1975(450), 1977(0), 1991(1045), 1999(0), 2006(2043) 2030(2538), 2030(2387), 2082 (0)	1936(0), 1937(0), 1947(9), 1947(9), 1954(284), 1954(284), 1955(259), 1972(472), 1972(472), 1976(0), 1992(903), 2001(0), 2010(2122) 2031(2420), 2031(2420), 2083(0)
BP86/ LANL2DZ	1860(0), 1871(14), 1872(4), 1875(5), 1884(242), 1886(102), 1887(325), 1895(338), 1905(0), 1905(368), 1916(1947), 1924(0), 1931 (631) 1955(1878), 1956(2072), 1999 (0)	1865(0), 1870(0), 1876(6), 1876(6), 1884(268), 1886(268), 1886(207), 1902(447), 1902(447), 1905(0), 1919(1929), 1927(0), 1937 (1025) 1957(1893), 1957(1893), 2002(0)
MPW1PW91/ LANL2DZ	1970(0), 1979(17), 1982(5), 1985(2), 1995(339), 1995(133), 1997(392), 2004(299), 2017(373), 2019(0), 2032(1811), 2039(0), 2044 (1474) 2072(2463), 2072(2714), 2124 (0)	1976(0), 1978(0), 1987(0), 1987(0), 1995(341), 1995(341), 1995(272), 2013(486), 2013(486), 2018(0), 2033(1117), 2043(0), 2052 (2020) 2074(2463), 2074(2463), 2128 (0)
Expet.[a, b]	1993(sh)，2000(w), 2018.5(w), 2036.5(s), 2054(m), 2075.5(vs)	

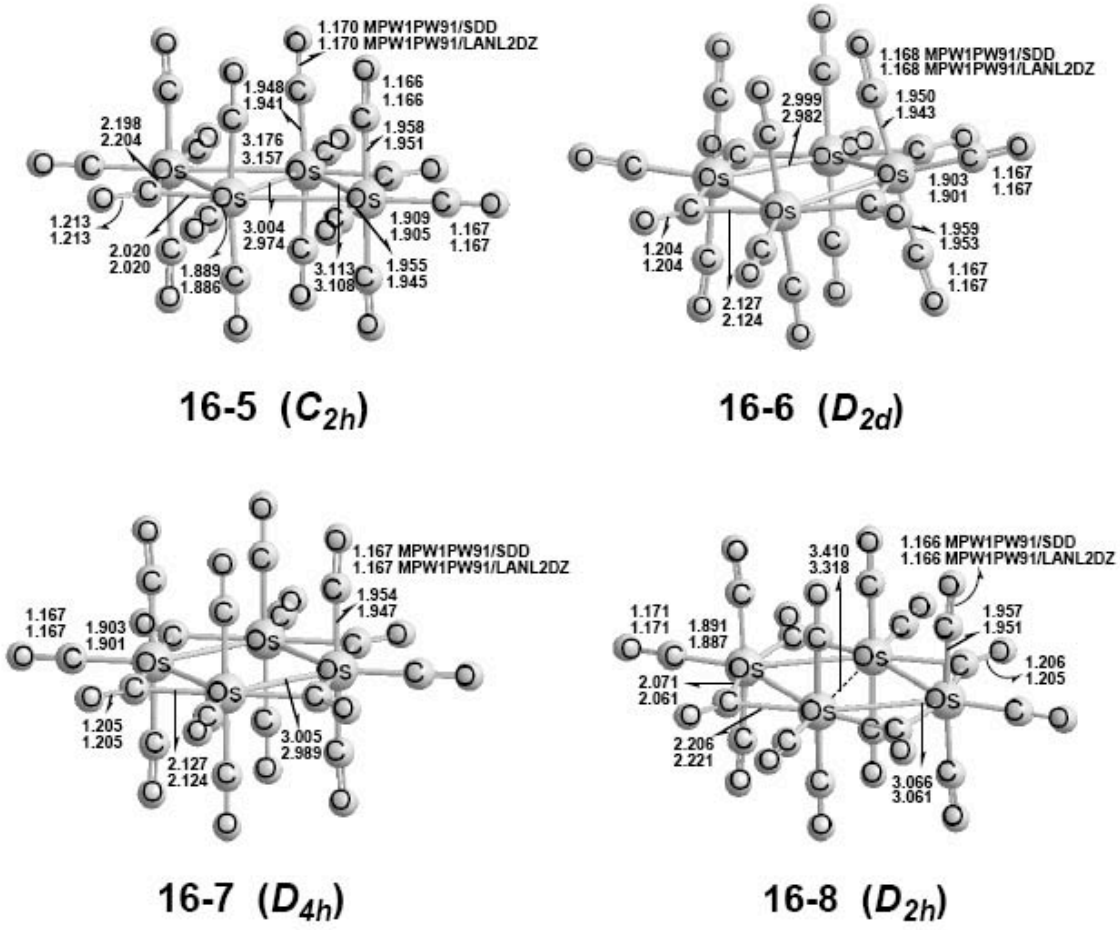


Figure S2. The four optimized structures of $Os_4(CO)_{16}$ with bridging carbonyl groups.

Table S3. The total energies (E, in Hartree) and relative energies (ΔE, in kcal/mol) of the four optimized $Os_4(CO)_{16}$ structures with bridging carbonyl groups. The number of imaginary vibrational frequencies (Nimg) for each structure is also listed.

		16-5 (C_{2h})	**16-6** (D_{2d})	**16-7** (D_{4h})	**16-8** (D_{2h})
B3LYP/SDD	E	-2176.33324	-2176.30919	-2176.30888	-2176.30780
	ΔE	6.9	22	22.3	22.9
	Nimag	0	0	1(17i)	1(60i)
BP86/SDD	E	-2177.01143	-2176.99626	-2176.99554	-2176.99322
	ΔE	4.8	14.3	14.8	16.2
	Nimag	0	0	1(20i)	1(30i)
MPW1PW91/ SDD	E	-2175.89859	-2175.87978	-2175.87865	-2175.87800
	ΔE	4.9	16.7	17.4	17.8
	Nimag	1(9i)	0	1(19i)	1(22i)
B3LYP/ LANL2DZ	E	-2177.62600	-2177.59734	-2177.59700	-2177.59714
	ΔE	9.5	27.5	27.7	27.6
	Nimag	0	1(44i)	(33i,15i)	1(86i)
BP86/ LANL2DZ	E	-2178.20272	-2178.18389	-2178.18309	-2178.18140
	ΔE	7	18.8	19.3	20.4
	Nimag	1(8i)	1(13i)	1(17i)	1(59i)
MPW1PW91/ LANL2DZ	E	-2177.231611	-2177.20849	-2177.20724	-2177.20721
	ΔE	8.0	22.5	23.2	23.3
	Nimag	1(12i)	1(20i)	1(17i)	1(57i)

Table S4. The infrared □(CO) vibrational frequencies (cm^{-1}) predicted for the higher energy $Os_4(CO)_{16}$ isomers (infrared intensities in parentheses are in km/mol, bridging □(CO) frequencies are in **bold**).

	MPW1PW91/SDD	MPW1PW91/LANL2DZ
16-3 (D_4)	1955(0), 1978(92), 1978(6), 1978(6), 1980(0), 1990(268), 1990(268), 2003(258), 2003(258), 2015(0), 2022(3443), 2029(0), 2031(0) 2064(2733), 2064(2733), 2114(0)	1960(0), 1983(31), 1983(31), 1983(31), 1985(0), 1996(311), 1996(311), 2008(255), 2008(255), 2020(0), 2028(3490), 2034(0), 2037 (0) 2070(2715), 2070(2715), 2120(0)
16-4 (D_{4h})	1962(0), 1971(0), 1982(0), 1986(129), 1986(129), 1987(0), 1987(0), 2009(517), 2009(517), 2014(0), 2033(3374), 2035(0), 2038(0) 2068(2613), 2068(2613), 2120(0)	1969(0), 1977(0), 1988(0), 1991(147), 1991(147), 1994(0), 1994(0), 2016(564), 2016(564), 2020(0), 2041(3399), 2041(0), 2045(0) 2075(2567), 2075(2567), 2127(0)
16-5 (C_{2h})	**1735(1161), 1748(0),** 1966(0), 1975(141), 1985(166), 1989(0), 2012(875), 2016(0), 2018(0), 2036(779), 2037(0), 2042(3371), 2048(2040) 2057(0), 2089(2213), 2126(0)	**1742(1150), 1755(0),** 1973(0), 1981(131), 1990(176), 1994(0), 2019(937), 2023(0), 2023(0), 2042(729), 2043(0), 2048(3434), 2055 (2034) 2063(0), 2095(2273), 2133(0)
16-6 (D_{2d})	**1753(0), 1782(1375), 1782(1375), 1808(0),** 1979(0), 1993(54), 1993(54), 2016(1), 2029(338), 2029(338), 2039(3488), 2045(0), 2061(62) 2071(2284), 2071(2284), 2124(0)	**1758(0), 1787(1344), 1787(1344), 1811(0),** 1985(0), 1998(60), 1998(60), 2022(6), 2034(276), 2034(276), 2045(3491), 2051(0), 2068(87) 2078(2378), 2078(2378), 2131(0)
16-7 (D_{4h})	**1751(0), 1781(1394), 1781(1394), 1807(0),** 1974(0), 1997(0), 1997(0), 2015(0), 2029(379), 2029(379), 2039(3581), 2046(0), 2062 (0) 2073(2285), 2073(2285), 2125(0)	**1756(0), 1786(1365), 1786(1365), 1809(0),** 1980(0), 2003(0), 2003(0), 2019(0), 2035(338), 2035(338), 2046(3620), 2052(0), 2068(0) 2079(2359), 2079(2359), 2132(0)
16-8 (D_{2h})	**1751(0), 1764(1764), 1775(1238), 1802(0),** 1983(0), 1985(0), 2009(0), 2015(0), 2018(1151), 2031(102), 2041(3620), 2049(0), 2073 (0) 2078(1936), 2083(1993), 2128(0)	**1758(0), 1771(1712), 1781(1219), 1807(0),** 1989(0), 1990(1), 2017(0), 2021(0), 2024(1192), 2035(98), 2048(3680), 2054(0), 2080(0) 2086(1934), 2089(2004), 2135(0)

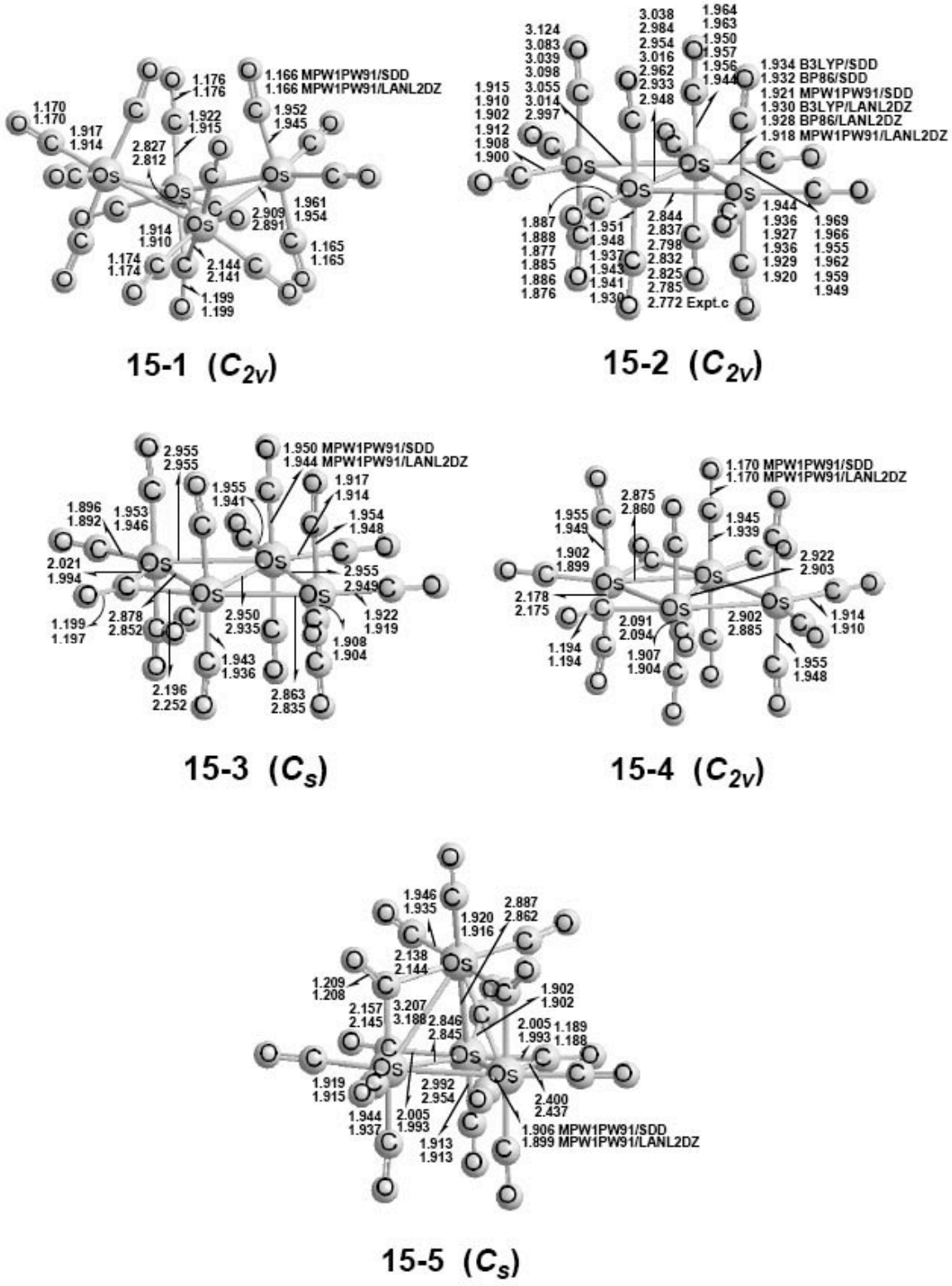


Figure S3. The five optimized structures of $Os_4(CO)_{15}$.

Table S5. The total energies (E, in Hartree) and relative energies (ΔE, in kcal/mol) of the five optimized structures of $Os_4(CO)_{15}$. The number of imaginary vibrational frequencies (Nimg) for each structure is also listed.

	15-1 (C_{2v})	**15-2** (C_{2v})	**15-3**(C_s)	**15-4**(C_{2v})	**15-5**(C_s)
MPW1PW91/SDD					
E	-2062.62207	-2062.62066	-2062.62355	-2062.62372	-2062.58802
ΔE	0	0.9	-0.9	-1.0	21.4
Nimag	0	0	0	0	1(57i)
MPW1PW91/LANL2DZ					
E	-2063.96144	-2063.96043	-2063.96032	-2063.95937	-2063.92194
ΔE	0	0.6	0.7	1.3	24.8
Nimag	0	0	0	1(23i)	2(58i,16i)

Table S6. The infrared □(CO) vibrational frequencies (cm^{-1}) predicted for isomer **15-2** of $Os_4(CO)_{15}$ (infrared intensities in parentheses are in km/mol).

	15-2 (C_{2v})
B3LYP / SDD	1898(177), 1919(249), 1940(7), 1944(43), 1948(13), 1963(0), 1965(487), 1969(617), 1976(311), 1976(644), 1915(2538), 1994(3148), 2015(1456), 2030(2400), 2078 (2)
BP86/ SDD	1826(152), 1856(140), 1870(52), 1873(25), 1878(5), 1886(0), 1895(538), 1895(773), 1904(58), 1908(343), 1914(546), 1915(2538), 1942(1220), 1956(1934), 1997 (1)
MPW1PW91/ SDD	1934(207), 1959(238), 1981(8), 1983(39), 1988(3), 2003(0), 2005(325), 2010(793), 2018(1047), 2018(217), 2029(529), 2035(3221), 2057(1456), 2074(2338), 2121 (1)
B3LYP / LANL2DZ	1904(182), 1923(254), 1946(9), 1951(55), 1953(10), 1969(0), 1971(448), 1974(711), 1982(242), 1982(861), 1994(559), 2001(3158), 2022(1386), 2037(2335), 2084 (2)
BP86/ LANL2DZ	1833(156), 1861(144), 1877(62), 1879(23), 1883(1), 1893(0), 1901(815), 1902(518), 1910(37), 1914(315), 1919(738), 1922(2546), 1949(1174), 1963(1894), 2003 (2)
MPW1PW91/ LANL2DZ	1940(213), 1963(242), 1987(10), 1990(54), 1994(1), 2009(0), 2012(288), 2015(894), 2024(150), 2025(1140), 2034(545), 2042(3257), 2065(1396), 2081(2272), 2129 (2)
Expet.[c]	1939(m, br), 2002(sh), 2023(m), 2045(vs), 2074(m), 2086(s)

Table S7. The infrared □(CO) vibrational frequencies (cm^{-1}) predicted for the five optimized $Os_4(CO)_{15}$ isomers (infrared intensities in parentheses are in km/mol, bridging □(CO) frequencies are in **bold**).

	MPW1PW91/SDD	MPW1PW91/LANL2DZ
15-1 (C_{2v})	**1792(551),** 1968(387), 1971(0), 1972(0), 1975(291), 1996(73), 2008(358), 2010(0), 2020 (37) 2028(314), 2030(1112), 2034(3410), 2043(1571), 2083(2431), 2117(81)	**1797(523),** 1974(387), 1978(0), 1978(0), 1981(310), 2002(102), 2014(408), 2016(0), 2026 (68) 2033(295), 2036(1010), 2040(3421), 2049(1687), 2089(2390), 2124(83)
15-3 (C_s)	**1828(607),** 1944(500), 1960(28), 1980(133), 1987(353), 1991(330), 1997(56), 2000(414), 2014(519), 2026(93), 2034(3367), 2043(857), 2057(1104), 2073(2239), 2121 (54)	**1846(547),** 1964(40), 1968(373), 1987(180), 1991(414), 1995(308), 2003(42), 2004(410), 2021(499), 2032(118), 2042(3358), 2047(866), 2063(1137), 2079(2217), 2128 (59)
15-4 (C_{2v})	**1824(1167), 1857(556),** 1968(0), 1969(15), 1989(146), 1994(290), 2001(53), 2006(516), 2009(692), 2025(71), 2033(3538), 2048(1976), 2050(66), 2079(2026), 2121 (39)	**1828(1157), 1859(552),** 1974(0), 1975(13), 1995(131), 2000(262), 2007(49), 2012(528), 2015(722), 2031(84), 2040(3594), 2055 (1991), 2056 (52), 2086(2016), 2128(43)
15-5 (C_s)	**1700(618), 1763(665), 1847(653), 1894(139),** 1985(0), 1994(7), 2000(441), 2008(237), 2009(304), 2027(881), 2038(413), 2056 (2317) 2065(2374), 2069(2129), 2107(30)	**1708(628), 1771(642), 1863(573), 1905(127),** 1989(0), 2001(6), 2005(425), 2013(294), 2014 (304) 2033(917), 2042(406), 2063(2368), 2070(2419), 2076(2150), 2113(20)

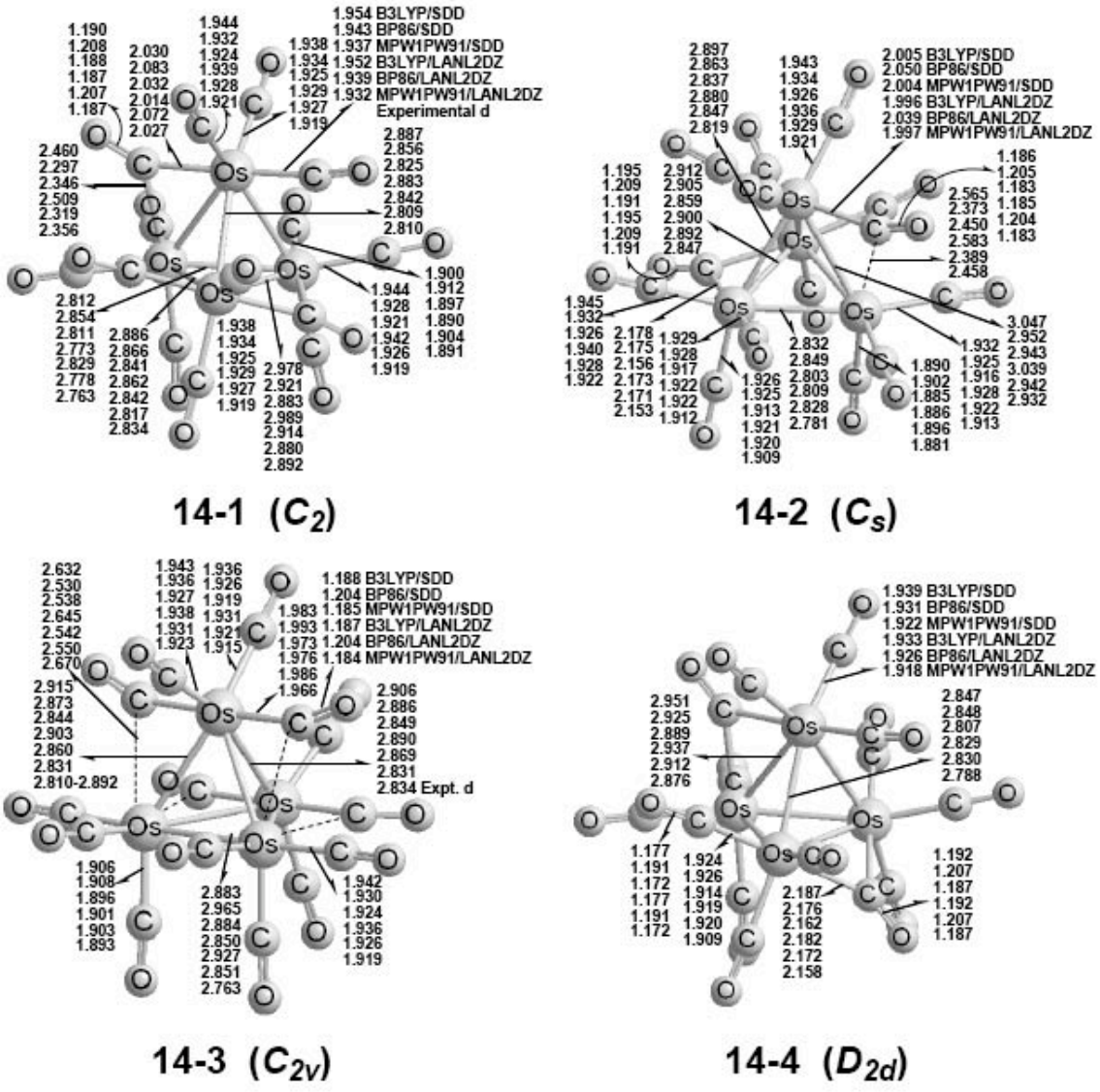


Figure S4. The four lowest lying optimized structures of $Os_4(CO)_{14}$.

Table S8. The total energies (E, in Hartree) and relative energies (ΔE, in kcal/mol) of the four lowest lying optimized structures of $Os_4(CO)_{14}$. The number of imaginary vibrational frequencies (Nimg) for each structure is also listed.

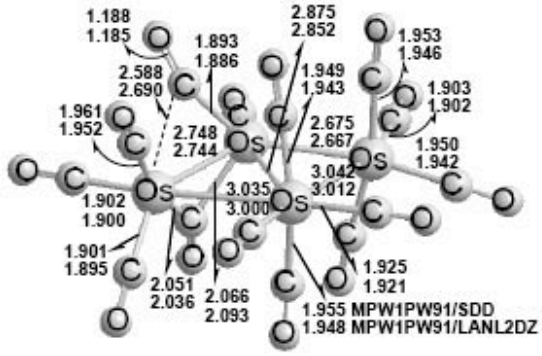
		14-1(C_2)	**14-2**($\mathbf{C_s}$)	**14-3**(C_{2v})	**14-4**(D_{2d})
B3LYP/SDD	E	-1949.69837	-1949.69823	-1949.69614	-1949.69587
	ΔE	0	0.09	1.3	1.5
	Nimag	0	0	1(16i)	2(16i,16i)
BP86/SDD	E	-1950.37018	-1950.37000	-1950.36816	-1950.36960
	ΔE	0	0.11	1.2	0.2
	Nimag	0	0	1(13i)	2(14i,14i)
MPW1PW91/ SDD	E	-1949.33904	-1949.33850	-1949.33771	-1949.3367
	ΔE	0	0.3	0.8	1.5
	Nimag	0	1(15i)	2(10i,3i)	2(37i,37i)
B3LYP/ LANL2DZ	E	-1950.99738	-1950.9971	-1950.99444	-1950.99451
	ΔE	0	0.18	1.7	1.6
	Nimag	0	0	1(15i)	2(53i,53i)
BP86/ LANL2DZ	E	-1951.56742 (99590)	-1951.56742	-1951.56474	-1951.56697
	ΔE	0	0.02	1.7	0.3
	Nimag	0	1(6i)	1(16i)	2(16i,16i)
MPW1PW91/ LANL2DZ	E	-1950.67800	-1950.67770	-1950.67592	-1950.67593
	ΔE	0	0.2	1.3	1.3
	Nimag	0	1(12i)	1(13i)	2(38i,38i)

Table S9. The infrared □(CO) vibrational frequencies (cm^{-1}) predicted for isomers **14-1** and **14-2** of $Os_4(CO)_{14}$ (infrared intensities in parentheses are in km/mol, bridging □(CO) frequencies are in **bold**).

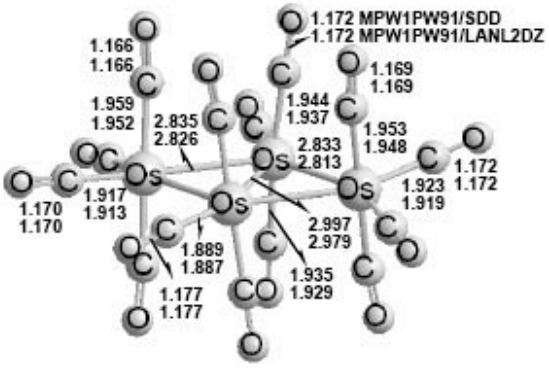
	14-1 (C_2)	**14-2** (C_s)
B3LYP/ SDD	**1854(2), 1859(825),** 1934(40), 1936(133), 1943(0), 1947(7), 1962(237), 1965(499), 1970(281), 1972(144), 1978(2283), 2008(2630), 2011(2699), 2054(9)	**1812(445), 1882(429),** 1934(92), 1937(121), 1946(2), 1949(95), 1959(212), 1968(412), 1971(153), 1972(157), 1996(2322), 2007(2761), 2011(2639), 2054(9)
BP86/ SDD	**1760(1), 1764(687),** 1868(87), 1869(195), 1876(13), 1876(7), 1886(155), 1896(313), 1901(253), 1901(47), 1922(1848), 1935(2292), 1935(2151), 1973(19)	**1750(311), 1781(381),** 1867(126), 1869(193), 1875(2), 1878(31), 1885(133), 1898(180), 1899(89), 1900(319), 1921(1783), 1933(2327), 1936(2199), 1972(14)
MPW1PW91/ SDD	**1868(6), 1874(920),** 1975(98), 1977(2), 1983(58), 1991(1), 2002(236), 2004(471), 2015(299), 2019(152), 2042(2558), 2053(2564), 2054(2744), 2100(28)	**1848(456), 1906(491),** 1975(72), 1979(134), 1988(39), 1989(1), 2000(198), 2008(382), 2014(153), 2014(222), 2039(2482), 2049(2847), 2054(2710), 2098(16)
B3LYP/ LANL2DZ	**1875(22), 1879(750),** 1938(78), 1940(231), 1946(14), 1953(2), 1968(104), 1971(566), 1975(266), 1977(254), 2003(2120), 2014(2716), 2017(2679), 2060(0)	**1817(434), 1892(398),** 1940(135), 1942(148), 1952(2), 1954(102), 1965(183), 1974(423), 1977(158), 1977(197), 2003(2279), 2014(2749), 2017(2659), 2060(4)
BP86/ LANL2DZ	**1768(0), 1772(669),** 1873(129), 1874(217), 1881(2), 1882(6), 1893(129), 1903(273), 1906(64), 1907(350), 1928(1778), 1941(2184), 1941(2297), 1979(12)	**1754(310), 1789(360),** 1873(156), 1875(210), 1881(1), 1884(20), 1892(122), 1905(151), 1905(87), 1907(404), 1928(1753), 1940(2319), 1942(2210), 1979(9)
MPW1PW91/ LANL2DZ	**1881(0), 1886(894),** 1983(45), 1983(121), 1990(21), 1996(8), 2009(204), 2012(513), 2021(316), 2022(194), 2048(2411), 2058(2690), 2060(2802), 2106(13)	**1853(448), 1915(465),** 1981(114), 1985(157), 1994(37), 1994(4), 2007(166), 2015(418), 2020(198), 2020(222), 2046(2425), 2057(2859), 2060(2760), 2105(8)
Experimental	1938(vw,br), 2018(m), 2058(s)	

Table S10. The infrared □(CO) vibrational frequencies (cm^{-1}) predicted for isomers **14-3** and **14-4** of $Os_4(CO)_{14}$ (infrared intensities in parentheses are in km/mol, bridging □(CO) frequencies are in **bold**).

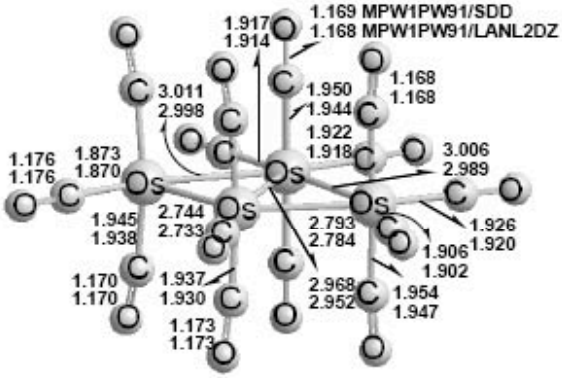
	14-3 (C_{2v})	**14-4** (D_{2d})
B3LYP/ SDD	**1858(0), 1877(977),** 1892(59), 1908(110), 1936(0), 1950(51), 1958(292), 1965(171), 1973(382), 1983(235), 2001(2684), 2015(2417), 2015(2222), 2058(43)	**1832(0), 1834(959),** 1937(262), 1937(262), 1944(0), 1948(0), 1955(0), 1970(72), 1970(72), 1972(302), 1992(2351), 2007(2922), 2007(2922), 2052(0)
BP86/ SDD	**1775(0), 1793(883),** 1811(65), 1826(122), 1872(0), 1878(134), 1889(130), 1892(220), 1904(216), 1914(132), 1924(2226), 1938(1948), 1947(1757), 1979(100)	**1760(0), 1761(705),** 1869(269), 1869(269), 1874(0), 1878(0), 1883(0), 1898(37), 1898(37), 1902(416), 1919(1707), 1933(2379), 1933(2379), 1971(0)
MPW1PW91/ SDD	**1880(0), 1901(1155),** 1916(86), 1936(156), 1981(0), 1992(102), 2004(223), 2006(161), 2018(353), 2030(243), 2044(2737), 2059(2425), 2063(2275), 2104(72)	**1870(0), 1871(997),** 1979(246), 1979(246), 1986(0), 1989(0), 1997(0), 2011(240), 2013(93), 2013(93), 2036(2481), 2049(3024), 2049(3024), 2096(0)
B3LYP/ LANL2DZ	**1869(0)**, **1887(897),** 1901(54), 1916(98), 1941(0), 1957(34), 1962(376), 1972(176), 1978(428), 1986(262), 2008(2649), 2019(2206), 2021(2433), 2064(29)	**1836(0), 1837(928),** 1943(299), 1943(299), 1949(0), 1954(0), 1960(0), 1977(66), 1977(66), 1979(310), 1998(2379), 2014(2896), 2014(2896), 2059(0)
BP86/ LANL2DZ	**1785(0), 1802(840),** 1819(63), 1834(119), 1878(0), 1885(117), 1897(134), 1897(268), 1910(270), 1918(147), 1932(2187), 1946(1963), 1951(1745), 1985(81)	**1763(0), 1764(683),** 1875(297), 1875(297), 1880(0), 1885(0), 1889(0), 1905(33), 1905(33), 1910(434), 1925(1718), 1940(2364), 1940(2364), 1978(0)
MPW1PW91/ LANL2DZ	**1891(0)**, **1911(1085),** 1926(84), 1944(153), 1987(0), 1999(80), 2008(299), 2013(161), 2024(427), 2033(269), 2052(2696), 2066(2272), 2066(2458), 2111(53)	**1873(0), 1874(969),** 1985(290), 1985(290), 1992(0), 1996(0), 2003(0), 2019(259), 2020(85), 2020(85), 2043(2511), 2057(3012), 2057(3012), 2104(0)
Experimental	1938(vw, br), 2018(m), 2058(s)	



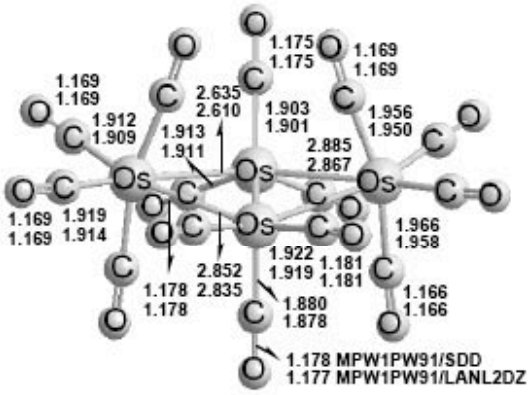
14-5 (C_1)



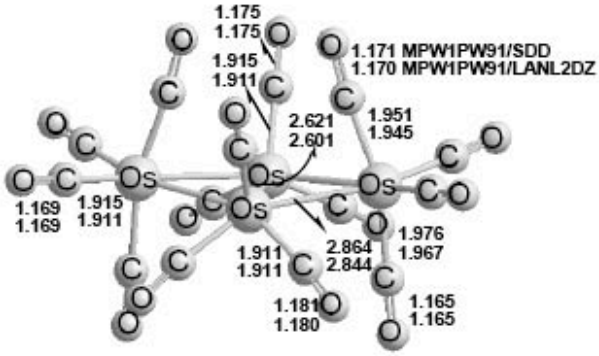
14-6 (C_2)



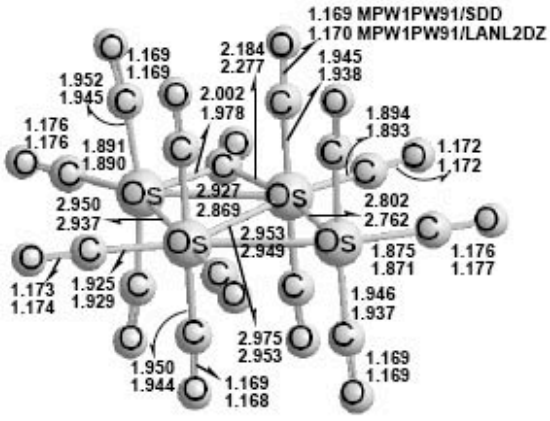
14-7 (C_s)



14-8 (C_s)



14-9 (C_{2v})



14-10 (C_s)

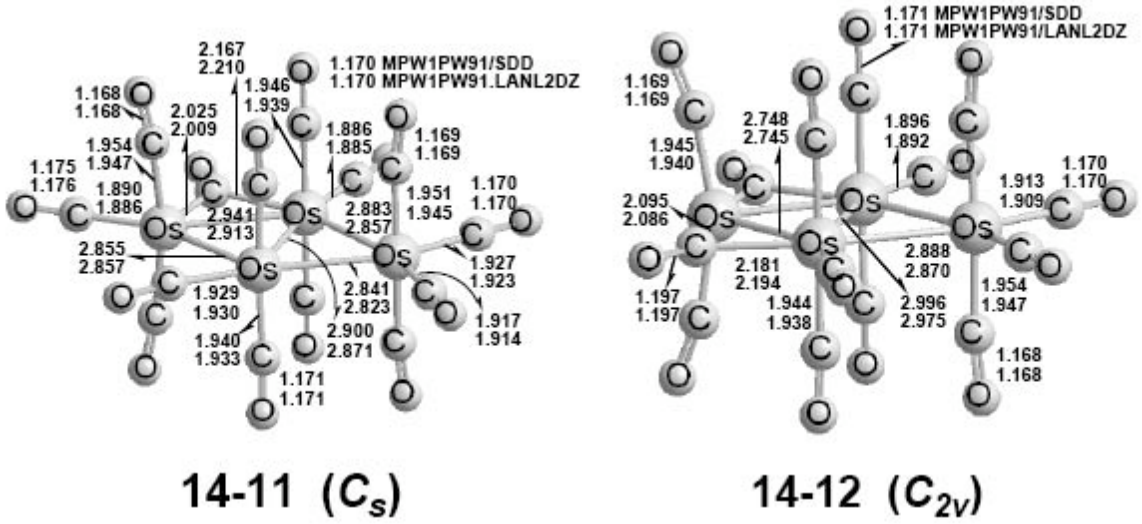


Figure S5. Eight butterfly isomers of $Os_4(CO)_{14}$.

Table S11. The total energies (E, in Hartree) and relative energies (ΔE, in kcal/mol) of structures **14-5** to **14-9** of $Os_4(CO)_{14}$. The number of imaginary vibrational frequencies (Nimg) for each structure is also listed.

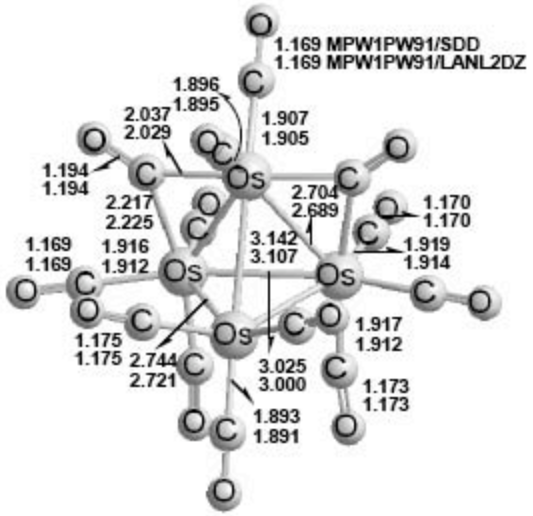
		14-5(C_1)	**14-6**(C_2)	**14-7**(C_s)	**14-8**(C_s)	**14-9**(C_{2v})
MPW1PW91/ SDD	E	-1949.33226	-1949.29588	-1949.29685	-1949.29478	-1949.29445
	ΔE	4.3	27.1	26.4	27.8	28.0
	Nimag	0	0	0	1(10i)	1(24i)
MPW1PW91/ LANL2DZ	E	-1950.66978	-1950.63554	-1950.63440	-1950.63582	-1950.63513
	ΔE	5.2	26.6	27.4	26.5	26.9
	Nimag	0	0	0	1(13i)	1(28i)

Table S12. The total energies (E, in Hartree) and relative energies (ΔE, in kcal/mol) of structures **14-10** to **14-1**2 of $Os_4(CO)_{14}$. The number of imaginary vibrational frequencies (Nimg) for each structure is also listed.

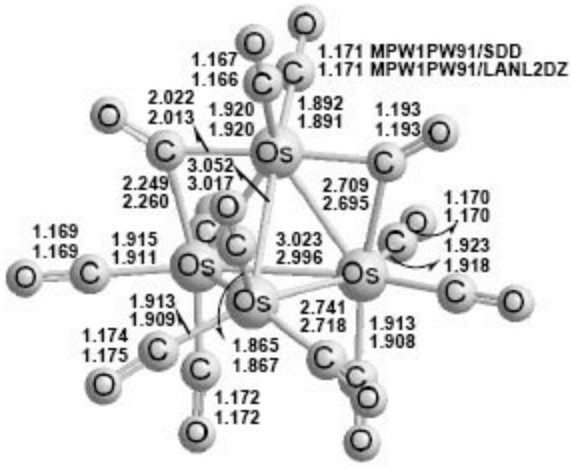
		14-10(C_s)	**14-11**(C_s)	**14-12**(C_{2v})
MPW1PW91/ SDD	E	-1949.29371	-1949.28839	-1949.28069
	ΔE	28.4	31.8	36.6
	Nimag	0	0	0
MPW1PW91/ LANL2DZ	E	-1950.62921	-1950.62420	-1950.61444
	ΔE	30.6	33.8	39.9
	Nimag	0	0	0

Table S13. The infrared □(CO) vibrational frequencies (cm^{-1}) predicted for the higher energy $Os_4(CO)_{14}$ structures (infrared intensities in parentheses are in km/mol, bridging □(CO) frequencies are in **bold**).

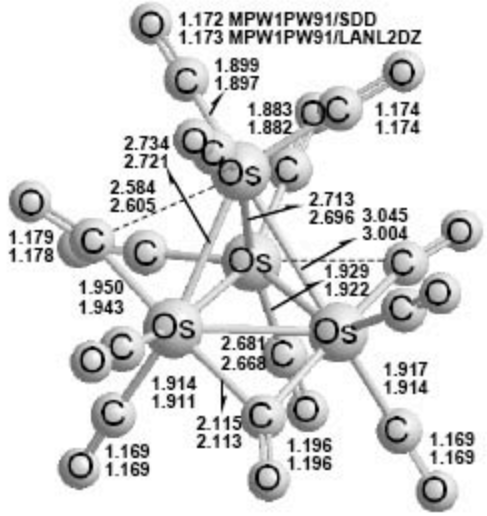
	MPW1PW91/SDD	MPW1PW91/LANL2DZ
14-5 (C_1)	**1787(306), 1904(317),** 1984(220), 1987(42), 1989(188), 2003(228), 2006(67), 2012(1097), 2018(339), 2027(2294), 2034(1175), 2060(975), 2073(2570), 2110(70)	**1798(296), 1928(291),** 1991(202), 1992(29), 1996(165), 2009(146), 2010(251), 2018(1030), 2025(433), 2033(2283), 2040(1218), 2066(974), 2078(2567), 2117(82)
14-6 (C_2)	1943(11), 1949(259), 1968(675), 1971(61), 1994(415), 2001(223), 2006(393), 2008(374), 2026(494), 2029(2933), 2033(2902), 2035(1), 2074(1953), 2119(55)	1949(14), 1954(271), 1973(674), 1977(62), 2001(402), 2007(147), 2012(339), 2015(357), 2031(452), 2035(3043), 2039(2995), 2041(3), 2081(1994), 2125(47)
14-7 (C_s)	1931(11), 1953(455), 1961(135), 1965(562), 1988(223), 1988(67), 1993(843), 2012(288), 2020(269), 2028(3122), 2030(569), 2052(1511), 2066(2077), 2116(76)	1938(0), 1963(542), 1967(71), 1971(611), 1993(339), 1995(35), 1998(744), 2019(306), 2026(309), 2035(558), 2036(3148), 2059(1539), 2072(1964), 2122(82)
14-8 (C_s)	1928(61), 1939(676), 1946(131), 1952(202), 1983(325), 1993(35), 2000(15), 2016(2), 2022(2795), 2028(233), 2030(2505), 2036(568), 2076(2972), 2108(1)	1936(60), 1947(665), 1953(141), 1959(203), 1991(309), 2002(48), 2007(7), 2022(5), 2029(2962), 2034(264), 2037(2392), 2042(607), 2083(2919), 2116(1)
14-9 (C_{2v})	1936(0), 1936(232), 1943(268), 1944(522), 1988(10), 1992(230), 1994(177), 2015(0), 2023(3227), 2026(2090), 2031(332), 2035(546), 2078(2789), 2108(1)	1945(0), 1939(676), 1951(234), 1952(538), 1998(210), 2002(31), 2003(104), 2020(0), 2029(3322), 2035(2349), 2036(367), 2041(360), 2084(2733), 2115(0)
14-10 (C_s)	**1805(468),** 1945(237), 1956(165), 1977(159), 1980(1), 1984(62), 1989(629), 1995(1072), 2014(219), 2028(3522), 2043(46), 2053(1307), 2064(2093), 2115(3)	**1841(462),** 1957(158), 1978(541), 1981(214), 1987(190), 1988(9), 1990(312), 1998(1233), 2017(144), 2034(3489), 2046(40), 2059(1423), 2068(1982), 2121(1)
14-11 (C_s)	**1807(505),** 1943(604), 1950(31), 1967(0), 1991(319), 1992(17), 1997(389), 1999(798), 2012(145), 2024(3676), 2037(525), 2047(1087), 2067(2363), 2114(19)	**1824(505),** 1947(604), 1956(30), 1971(2), 1995(411), 1999(26), 2002(336), 2005(754), 2018(152), 2031(3706), 2044(483), 2052(1114), 2074(2313), 2121(27)
14-12 (C_{2v})	**1807(1169), 1856(679),** 1942(140), 1963(0), 1979(389), 1984(225), 1991(2), 2006(714), 2020(90), 2023(3261), 2038(13), 2045(1944), 2060(1703), 2115(157)	**1810(1150), 1858(691),** 1949(87), 1968(0), 1986(392), 1989(206), 1996(1), 2012(701), 2026(96), 2030(3350), 2045(1), 2051(2011), 2068(1647), 2121(159)



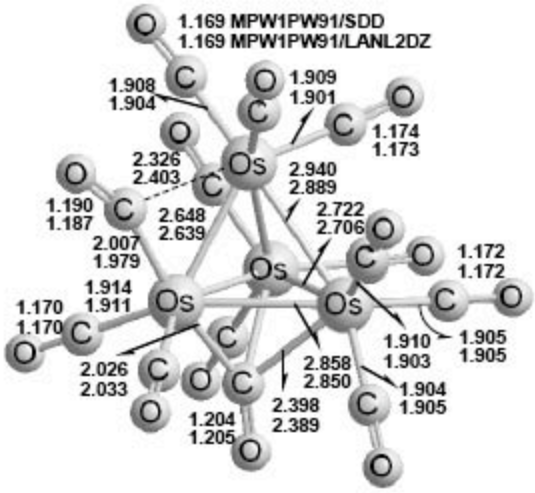
13-1 (C_s)



13-2 (C_s)



13-3 (C_2)



13-4 (C_s)

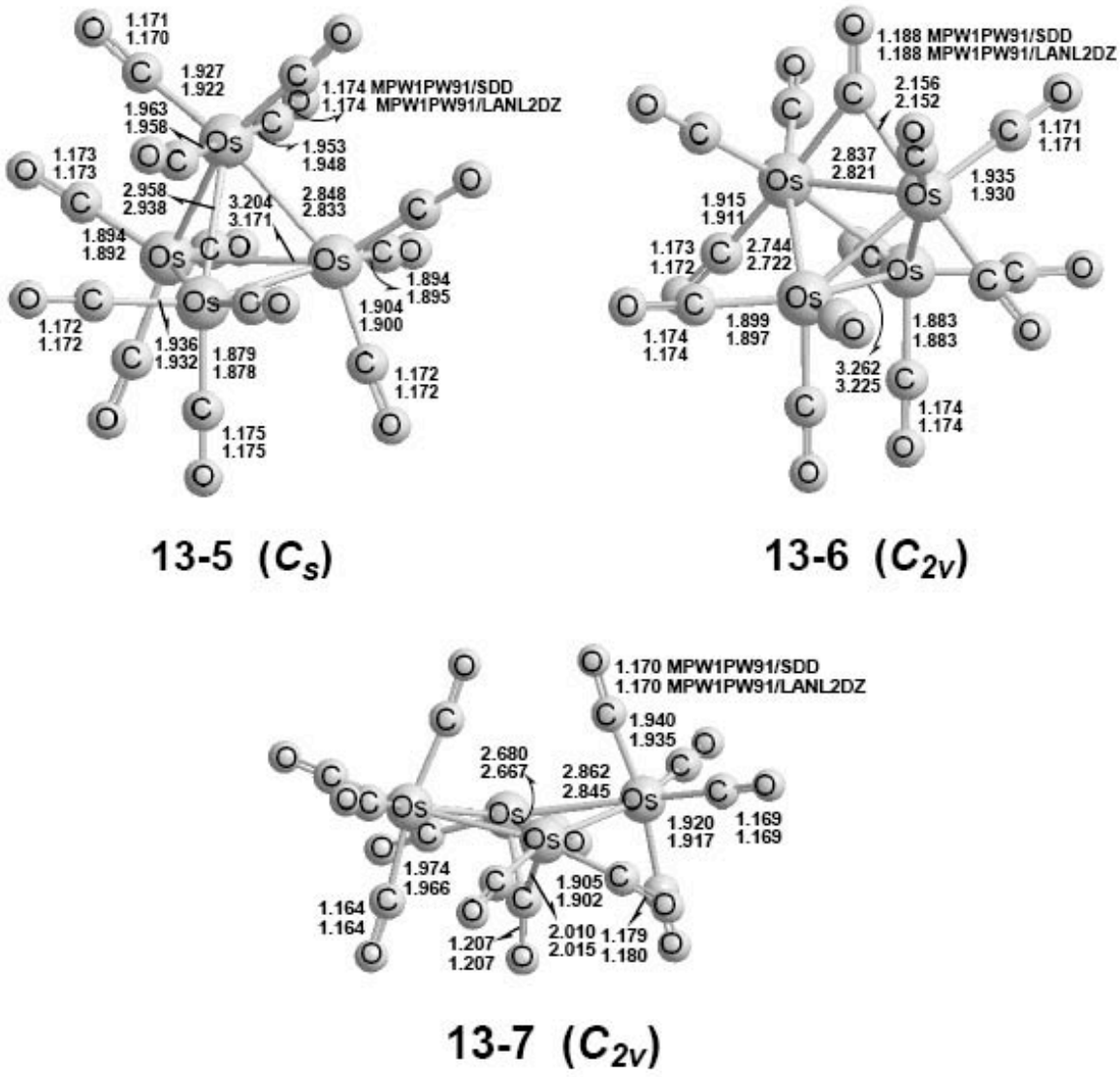


Figure S6. The seven optimized structures of $Os_4(CO)_{13}$.

Table S14. The total energies (E, in Hartree) and relative energies (ΔE, in kcal/mol) of the four lowest lying optimized structures of $Os_4(CO)_{13}$. The number of imaginary vibrational frequencies (Nimg) for each structure is also listed.

		13-1 (C_s)	**13-2** (C_s)	**13-3** (C_2)	**13-4** (C_s)
MPW1PW91/ SDD	E	-1836.03282	-1836.03082	-1836.02950	-1836.02407
	ΔE	0	1.3	2.1	5.5
	Nimag	0	1(9i)	1(37i)	1(19i)
MPW1PW91/ LANL2DZ	E	-1837.37054	-1837.36841	-1837.36782	-1837.36118
	△E	0	1.3	1.7	5.9
	Nimag	0	1(11i)	1(29i)	1(26i)

Table S15. The total energies (E, in Hartree) and relative energies (ΔE, in kcal/mol) of the three remaining optimized structures of $Os_4(CO)_{13}$. The number of imaginary vibrational frequencies (Nimg) for each structure is also listed.

		13-5 (C_s)	**13-6** (C_{2v})	**13-7** (C_{2v})
MPW1PW91/ SDD	E	-1836.01625	-1836.00767	-1835.98721
	ΔE	10.4	15.8	28.6
	Nimag	1(27i)	3(36i,27i,17i)	1(26i)
MPW1PW91/ LANL2DZ	E	-1837.35707	-1837.34800	-1837.32437
	ΔE	8.5	14.1	29
	Nimag	1(27i)	3(37i,27i,2i)	1(25i)

Table S16. The infrared □(CO) vibrational frequencies (cm^{-1}) predicted for the seven $Os_4(CO)_{13}$ optimized structures (infrared intensities in parentheses are in km/mol, bridging □(CO) frequencies are in **bold**).

	MPW1PW91/SDD	MPW1PW91/LANL2DZ
13-1 (C_s)	**1826(742), 1873(385),** 1975(269), 1977(229), 1979(9), 1997(242), 2006(20), 2013(625), 2018(614), 2043(2557), 2050(2525), 2052(2022), 2094(19)	**1834(712), 1878(381),** 1982(260), 1983(253), 1987(2), 2004(278), 2014(4), 2020(601), 2024(565), 2049(2639), 2057(2537), 2059(2049), 2101(23)
13-2 (Cs)	**1832(854), 1879(367),** 1968(307), 1969(181), 1986(0), 1999(230), 2004(50), 2015(269), 2017(563), 2039(2762), 2054(2391), 2058(2016), 2096(32)	**1842(813), 1885(364),** 1973(313), 1976(186), 1992(0), 2005(269), 2011(36), 2021(184), 2024(576), 2044(2853), 2060(2389), 2065(2038), 2103(39)
13-3 (C_2)	**1832(751),** 1942(241), 1952(69), 1978(147), 1982(21), 1991(318), 1999(1336), 2008(64), 2015(682), 2044(2377), 2050(1843), 2051(2328), 2092(1)	**1841(729),** 1953(159), 1963(71), 1982(158), 1986(39), 1997(334), 2003(1399), 2015(74), 2021(569), 2048(2506), 2056(2322), 2058(1872), 2099(7)
13-4 (C_s)	**1767(469), 1880(595),** 1972(24), 1985(43), 1989(0), 1990(392), 2002(264), 2018(841), 2019(565), 2045(2187), 2054(2370), 2056(2179), 2095(54)	**1767(423), 1907(554),** 1977(21), 1993(302), 1993(1), 1999(161), 2010(225), 2021(547), 2023(817), 2051(2279), 2058(2500), 2061(2183), 2102(40)
13-5 (C_s)	1948(190), 1969(52), 1971(122), 1977(249), 1979(15), 1994(352), 1995(651), 2007(61), 2008(428), 2038(2257), 2046(2822), 2047(2456), 2092(17)	1957(152), 1974(56), 1978(98), 1984(311), 1985(15), 2001(327), 2002(678), 2014(73), 2015(425), 2044(2300), 2052(2491), 2053(2777), 2099(16)
13-6 (C_{2v})	**1867(554)**, 1964(90), 1969(0), 1977(378), 1991(33), 2000(715), 2001(26), 2003(740), 2003(0), 2038(2063), 2042(2604), 2043(2960), 2089(41)	**1873(538)**, 1969(93), 1977(0), 1984(419), 1997(67), 2007(648), 2010(29), 2010(0), 2011(731), 2045(2085), 2047(2677), 2051(2947), 2096(26)
13-7 (C_{2v})	**1793(220)**, 1940(0), 1945(301), 1966(952), 1983(191), 1999(66), 2013(0), 2018(2993), 2026(1622), 2033(406), 2037(657), 2080(2801), 2110(0)	**1802(222)**, 1946(0), 1951(319), 1971(988), 1988(189), 1998(100), 2019(0), 2024(3018), 2035(1680), 2039(406), 2043(598), 2087(2744), 2118(1)
Expet[e]	1998w , 2014m , 2018m(sh), 2052s, 2064s, 2077s	

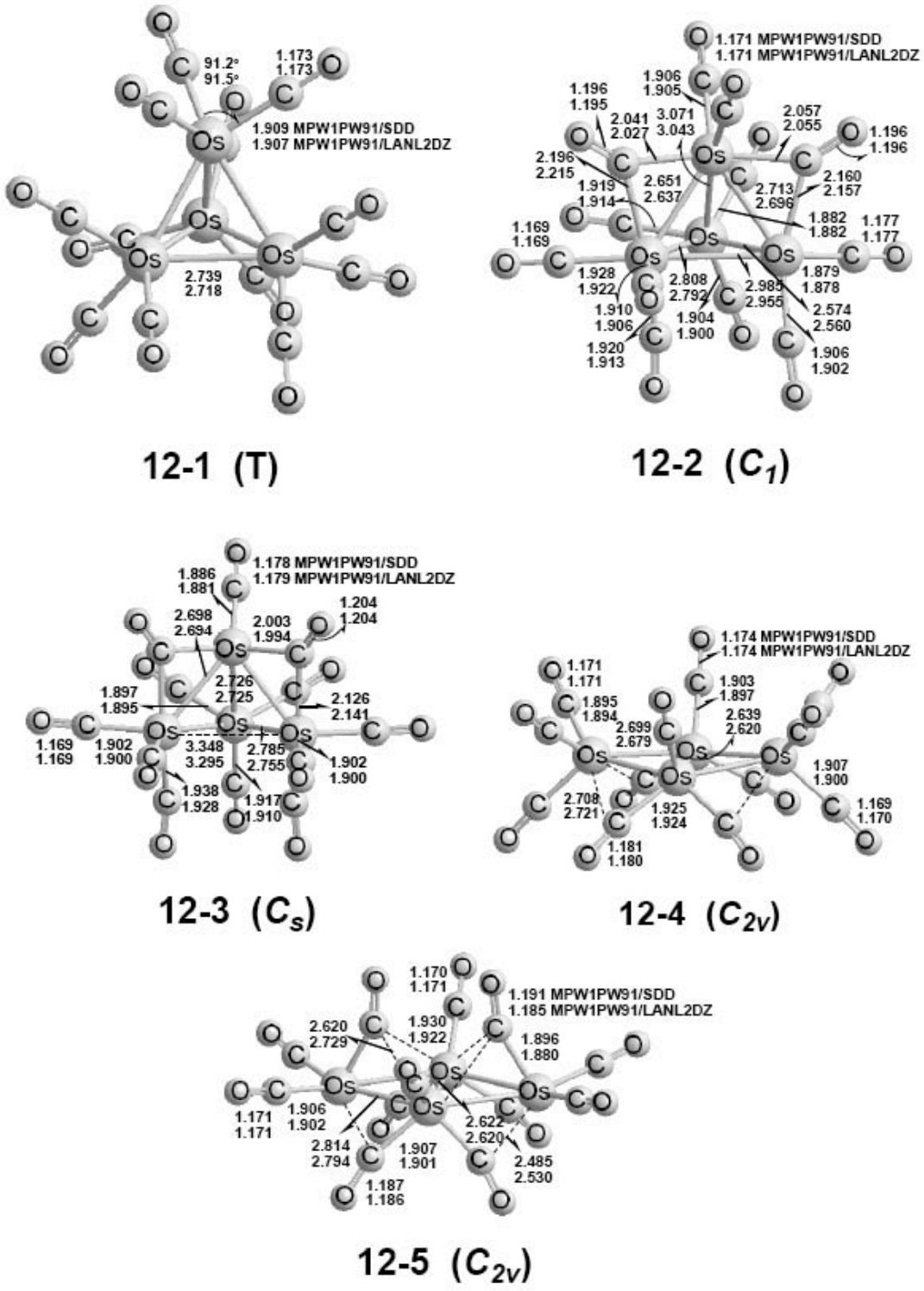


Figure S7. The five optimized structures found for $Os_4(CO)_{12}$.

Table S17. The total energies (E, in Hartree) and relative energies (ΔE, in kcal/mol) of $Os_4(CO)_{12}$. The number of imaginary vibrational frequencies (Nimg) for each structure is also listed.

	12-1 (*T*)	**12-2** (C_1)	**12-3** (C_s)	**12-4** (C_{2v})	**12-5** (C_{2v})
MPW1PW91/SDD					
E	-1722.71022	-1722.71086	-1722.70660	-1722.69677	-1722.69141
ΔE	0	-0.4	2.3	8.4	11.8
Nimag	0	0	0	0	3(43i, 29i, 21i)
MPW1PW91/LANL2DZ					
E	-1724.05171	-1724.04774	-1724.03979	-1724.03699	-1724.02382
ΔE	0	2.5	6.9	9.2	17.5
Nimag	0	0	0	0	1(50i)

Table S18. The infrared □(CO) vibrational frequencies (cm^{-1}) predicted for the $Os_4(CO)_{12}$ isomers (infrared intensities in parentheses are in km/mol, bridging □(CO) frequencies are in **bold**).

	MPW1PW91/SDD	MPW1PW91/LANL2DZ
12-1 (*T*)	1965(124), 1965(124), 1965(124), 1990(654), 1990(654), 1990(654), 2000(0), 2000(0), 2040(2557), 2040(2557), 2040(2557), 2089(0)	1973(128), 1973(128), 1973(128), 1997(681), 1997(681), 1997(681), 2007(0), 2007(0), 2046(2595), 2046(2595), 2046(2595), 2096(0)
12-2 (C_1)	**1814(759), 1860(499),** 1963(111), 1982(73), 1990(176), 1994(392), 2006(431), 2010(515), 2024(2834), 2045(2036), 2054(2038), 2090(121)	**1822(728), 1868(496),** 1971(129), 1990(28), 1996(163), 2001(466), 2012(410), 2016(497), 2030(2872), 2052(2080), 2059(2080), 2096(109)
12-3 (C_s)	**1770(317), 1798(1096),** 1958(7), 1963(914), 1977(98), 1995(53), 2008(613), 2008(1201), 2020(835), 2056(2338), 2056(2006), 2091(183)	**1775(330), 1804(1061),** 1969(2), 1970(894), 1984(104), 2001(29), 2013(623), 2015(1331), 2025(733), 2061(2376), 2061(2048), 2097(190)
12-4 (C_{2v})	1937(0), 1939(252), 1942(469), 1949(913), 1989(5), 2000(444), 2005(0), 2007(19), 2019(1991), 2020(3032), 2068(2737), 2092(30)	1948(0), 1951(243), 1954(456), 1959(825), 1995(36), 2007(697), 2010(0), 2010(22), 2024(1842), 2028(3050), 2072(2734), 2097(29)
12-5 (C_{2v})	**1875(13), 1899(0),** 1899(141), 1910(262), 1912(200), 1926(2087), 1997(749), 1999(0), 2016(192), 2024(2582), 2042(3847), 2073(117)	**1913(61), 1914(0),** 1920(100), 1924(206), 1936(992), 1955(1298), 2001(677), 2004(0), 2020(215), 2028(2691), 2047(3904), 2080(135)