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Heptacarbonyldiosmium and Hexacarbonyldiosmium: Two Highly Unsaturated Binuclear Osmium Carbonyls*

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Abstract. A total of nine singlet structures for $Os_2(CO)_7$ and 15 structures (nine singlet and six triplet) for $Os_2(CO)_6$ have been found by density functional theory thereby indicating very complicated energy surfaces. The global minimum for $Os_2(CO)_7$ is a doubly carbonyl bridged structure $Os_2(CO)_5(\mu\text{-}CO)_2$ with an Os=Os distance of 2.67 Å suggesting a formal double bond and hence a 16-electron rather than an 18-electron configuration for one of the osmium atoms. However, at only slightly higher energy (3.2 kcal mol^{-1}) lies an unbridged $Os_2(CO)_7$ structure with a shorter Os≡Os distance of 2.54 Å, corresponding to a formal triple bond and an 18-electron configuration for each osmium atom. The global minimum for $Os_2(CO)_6$ can be derived from that of $Os_2(CO)_7$ by removal of a carbonyl group while retaining the Os=Os double bond and the two bridging carbonyl groups. Slightly higher energy $Os_2(CO)_6$ structures at ≈3 kcal mol^{-1} or more above the global minimum have short Os≣Os distances around 2.4 Å, consistent with the formal quadruple bonds necessary to give both osmium atoms the favored 18-electron configuration. None of the 24 structures for $Os_2(CO)_7$ and $Os_2(CO)_6$ found in this work has a four-electron donor $\eta^2\text{-}\mu\text{-}CO$ bridging carbonyl group.

Keywords: DFT calculations, organometallic compounds, osmium carbonyls

INTRODUCTION

Osmium forms a greater variety of stable binary metal carbonyl derivatives than any other element. Isolable osmium carbonyl derivatives include the mononuclear $Os(CO)_5$ (Refs. 1,2), the binuclear $Os_2(CO)_9$ (Refs. 3,4), the trinuclear $Os_3(CO)_{12}$ (Ref. 5), the three tetranuclear derivatives $Os_4(CO)_n$ (n = 16,[6,7] 15,[8] 14[9]), and a number of additional binary osmium carbonyl derivatives of higher nuclearity. In addition, metastable unsaturated osmium carbonyl derivatives such as $Os(CO)_4$, $Os(CO)_3$, and $Os_2(CO)_8$ have been generated by photolysis of $Os(CO)_5$ in the gas phase[10] or by cocondensation of laser ablated osmium atoms with carbon monoxide in a low-temperature neon matrix.[11] The unsaturated $Os_2(CO)_8$ can be generated more selectively at low temperatures by the photolysis of a binuclear osmium carbonyl precursor[12,13] such as $Os_2(CO)_9$ or (C_2H_4)-$Os_2(CO)_8$.

The osmium carbonyl derivative $Os_2(CO)_8$ requires a formal Os=Os double bond if both osmium atoms have the favored 18-electron configuration and all eight carbonyl groups are the usual two-electron donors. Successive loss of carbonyl groups from $Os_2(CO)_8$ to give $Os_2(CO)_7$ and $Os_2(CO)_6$ should lead to formal Os≡Os triple bonds and Os≣Os quadruple bonds, respectively, if the 18-electron rule is followed and all carbonyl groups remain two-electron donors. The idea of Os≣Os quadruple bonds is *a priori* not an unusual one in view of the involvement of the neighboring third-row transition metal rhenium in the first example of metal-metal quadruple bonding, namely in the ion octachlororhenate(III), $Re_2Cl_8^{2-}$, discovered by Cotton and Harris in 1965.[14]

This paper describes our studies of the more highly unsaturated binuclear osmium carbonyls $Os_2(CO)_7$ and $Os_2(CO)_6$ using density functional theory (DFT) methods similar to those used in our previous research on the trinuclear osmium carbonyls $Os_3(CO)_n$ (n = 12, 11, 10, 9)[15] and the tetranuclear osmium carbonyls $Os_4(CO)_n$ (n = 16, 15, 14, 13, 12)[16] as well as $Os(CO)_n$ (n = 5, 4, 3) and $Os_2(CO)_n$ (n = 9, 8).[17] The resulting

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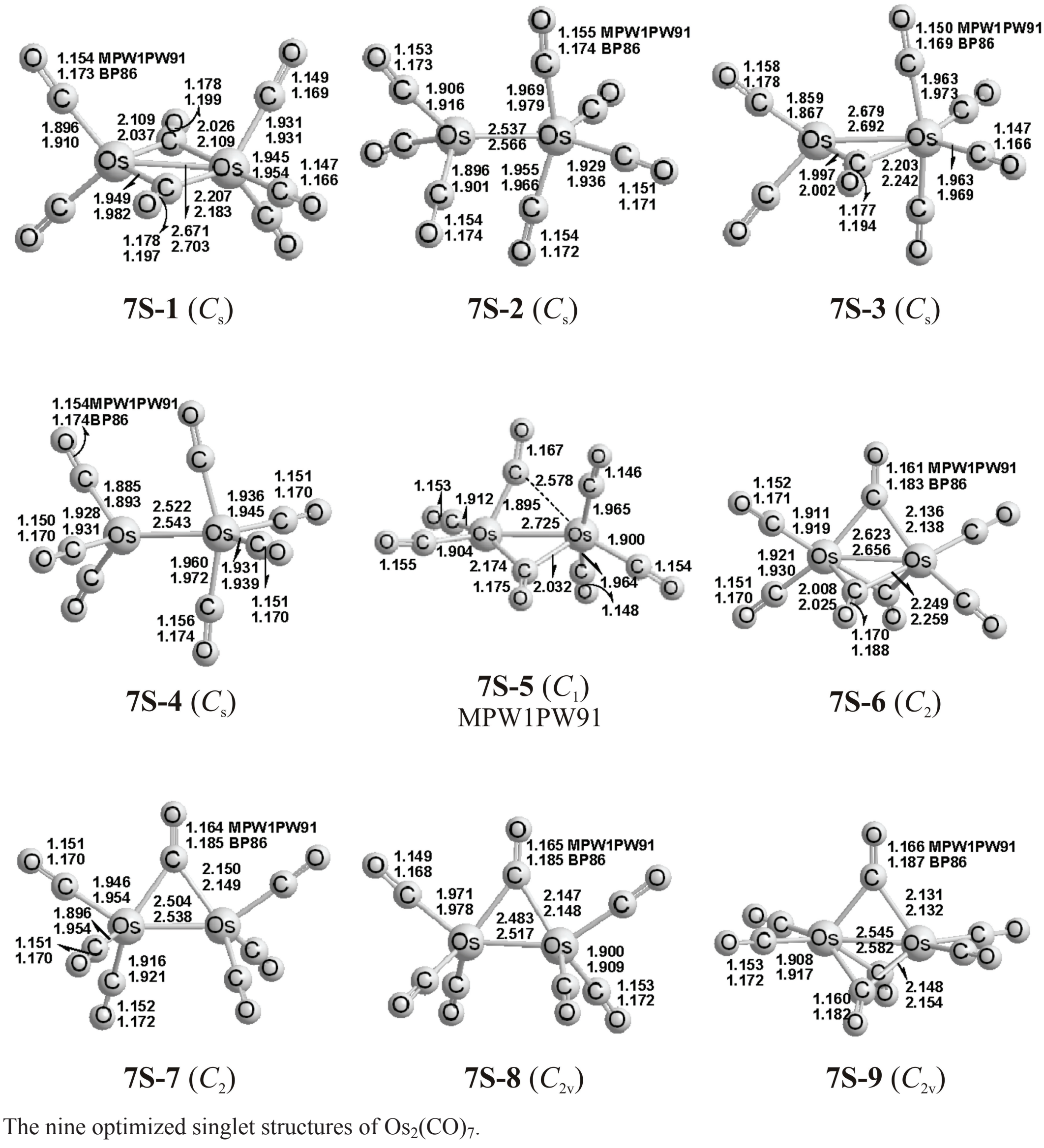
* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

** Authors to whom correspondence should be addressed. (E-mails: rbking@chem.uga.edu; qsli@scnu.edu.cn) potential energy surfaces are found to be rather complicated with nine singlet structures of $Os_2(CO)_7$ and a total of 15 singlet and triplet structures of $Os_2(CO)_6$ within 25 kcal mol^{-1} of the corresponding global minima.

THEORETICAL METHODS

Density functional theory methods (DFT) have been acknowledged to be a practical and effective tool for the computation of organometallic compounds.[18–25] Two DFT methods, namely BP86 and MPW1PW91, were used in the present study. The BP86 method is a pure DFT method that combines Becke's 1988 exchange functional with Perdew's 1986 correlation functional.[26,27] The BP86 method has been shown to be reliable for first-row transition metal organometallic systems.[28,29] The MPW1PW91 method[30] is a so-called second generation[31] functional, which combines the modified Perdew-Wang exchange functional with Perdew-Wang's 91 gradient-correlation functional.[32] The MPW1PW91 method has been found to be more suitable for geometry optimization of the second and third row transition metal systems,[33,34] while the BP86 method usually provides better vibrational frequencies.

For the third row transition metals, the large numbers of electrons may increase exponentially the computational efforts. In order to reduce the cost, effective core potential (ECP) relativistic basis sets are employed. The SDD (Stuttgart-Dresden ECP plus DZ)[35] ECP basis set was used for the osmium atoms. For the C and O atoms, double-ζ plus polarization (DZP) basis sets were used. The latter are Huzinaga-Dunning's contracted



7S-1 (C_s) **7S-2** (C_s) **7S-3** (C_s)

7S-4 (C_s) **7S-5** (C_1) MPW1PW91 **7S-6** (C_2)

7S-7 (C_2) **7S-8** (C_{2v}) **7S-9** (C_{2v})

Figure 1. The nine optimized singlet structures of $Os_2(CO)_7$.

double-ζ contraction sets[36,37] plus a set of spherical harmonic d polarization functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$, designated as (9s5p1d/4s2p1d).

The geometries of all structures were fully optimized using the two selected DFT methods with the SDD ECP basis sets. The vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates at the same theoretical levels. The corresponding infrared intensities were also evaluated analytically. The reported ν(CO) frequencies are those evaluated using the BP86 method since it is found to be more reliable than the MPW1PW91 method for such frequencies.

All computations were carried out with the Gaussian 03 program.[38] The fine (75, 302) grid is the default for evaluating integrals numerically. The finer (120, 974) grid[39] was used for re-examining the small imaginary vibrational frequencies. All of the predicted triplet structures are found to have negligible spin contamination, with $\langle \boldsymbol{S}^2 \rangle$ values within 0.04 of the ideal value of $S(S+1) = 2$.

RESULTS

$Os_2(CO)_7$

A total of thirteen structures were found for $Os_2(CO)_7$, namely nine singlets and four triplets. This plethora of $Os_2(CO)_7$ structures includes structures with zero, one, two or three bridging carbonyl groups indicating a complicated potential energy surface. All of the triplet structures of $Os_2(CO)_7$ are predicted to lie more than 20 kcal mol^{-1} in energy above the lowest lying singlet $Os_2(CO)_7$ structure. Therefore, the triplet structures of $Os_2(CO)_7$ are not discussed in this paper.

The global minimum predicted for $Os_2(CO)_7$ is an unsymmetrical singlet C_s structure **7S-1** with two bridging CO groups (Figure 1, Table 1). Its very small imaginary vibrational frequency of $3i$ cm^{-1} (BP86) is removed when a finer integration grid (120, 974) is used. The Os=Os bond distance is predicted at 2.671 Å (MPW1PW91) or 2.703 Å (BP86) corresponding to a double bond consistent with the favored 18-electron configuration for one osmium atom (the rightmost osmium atom depicted in Figure 1 bearing three terminal CO groups) but only a 16-electron configuration for the other osmium atom (the leftmost osmium atom depicted in Figure 1 bearing only two terminal CO groups). The theoretical ν(CO) frequencies at 1799 cm^{-1} and 1827 cm^{-1} (BP86, Table 3) for **7S-1** correspond to the two bridging CO groups**.**

The next higher energy singlet structure **7S-2** of $Os_2(CO)_7$ is a C_s unsymmetrical unbridged structure (Figure 1, Table 1), lying 3.2 kcal mol^{-1} (MPW1PW91) or 7.6 kcal mol^{-1} (BP86) above the global minimum **7S-1**. Structure **7S-2** is a genuine minimum, having all real vibrational frequencies. The Os≡Os distance in **7S-2** is 0.13 Å shorter than that in **7S-1,** suggesting a formal metal-metal triple bond. A zwitterionic formulation of **7S-2** gives both osmium atoms the favored 18-electron configuration with a formal negative charge on the $Os(CO)_3$ unit and a formal positive charge on the $Os(CO)_4$ unit, *i.e.* $(OC)_3Os^{-}{\equiv}Os^{+}(CO)_4$. Structure **7S-2** is related to the global minimum of $Fe_2(CO)_7$ predicted by a theoretical DFT study.[40]

The third genuine minimum found for $Os_2(CO)_7$ is also an C_s unsymmetrical structure **7S-3** (Figure 1, Table 1) but with one bridging carbonyl. Structure **7S-3** lies in energy above the global minimum **7S-1** by 4.2 kcal mol^{-1} (MPW1PW91) or 10.6 kcal mol^{-1} (BP86).

Table 1. Total energies (E / hartree), relative energies (ΔE / kcal mol^{-1}), number of imaginary vibrational frequencies (Nimag), and Os-Os bond distances / Å of the four lowest lying structures of $Os_2(CO)_7$

		7S-1 (C_s)	**7S-2** (C_s)	**7S-3** (C_s)	**7S-4** (C_s)
MPW1PW91	E	−974.93218	−974.92704	−974.92556	−974.92382
	ΔE	0	3.2	4.2	5.2
	Nimag	0	0	0	1 (44i)
	Os-Os	2.671	2.537	2.679	2.522
BP86	E	−975.41223	−975.40010	−975.39538	−975.39630
	ΔE	0	7.6	10.6	10.0
	Nimag	1 (3i)	0	0	1 (50i)
	Os-Os	2.703	2.566	2.692	2.543

Table 2. Total energies (E / hartree), relative energies (ΔE / kcal mol^{-1}), number of imaginary vibrational frequencies (Nimag), and Os-Os bond distances / Å of the higher energy structures of $Os_2(CO)_7$

		7S-5 (C_1)	**7S-6** (C_2)	**7S-7** (C_2)	**7S-8** (C_{2v})	**7S-9** (C_{2v})
MPW1PW91	E	−974.92262	−974.91623	−974.91413	−974.91309	−974.89947
	ΔE	6.0	10.0	11.3	12.0	20.5
	Nimag	0	1(111i)	1(147i)	1(26i)	1(70i)
	Os-Os	2.725	2.623	2.504	2.483	2.545
BP86	E	The same as **7-6** (C_2)	−975.39906	−975.39144	−975.39069	−975.38329
	ΔE		8.3	13.0	13.5	18.2
	Nimag		1(12i)[a]	1(69i)	1(23i)	1(56i)
	Os-Os		2.656	2.538	2.517	2.582

[a] This imaginary vibrational frequency is removed with the larger integration grid.

The Os=Os bond length in **7S-3** of 2.679 Å (MPW1PW91) or 2.692 Å (BP86) corresponds to a formal double bond giving the $Os(CO)_4$ osmium atom the favored 18-electron configuration and a formal positive charge and the $Os(CO)_2$ osmium atom a 16-electron configuration and a formal negative charge.

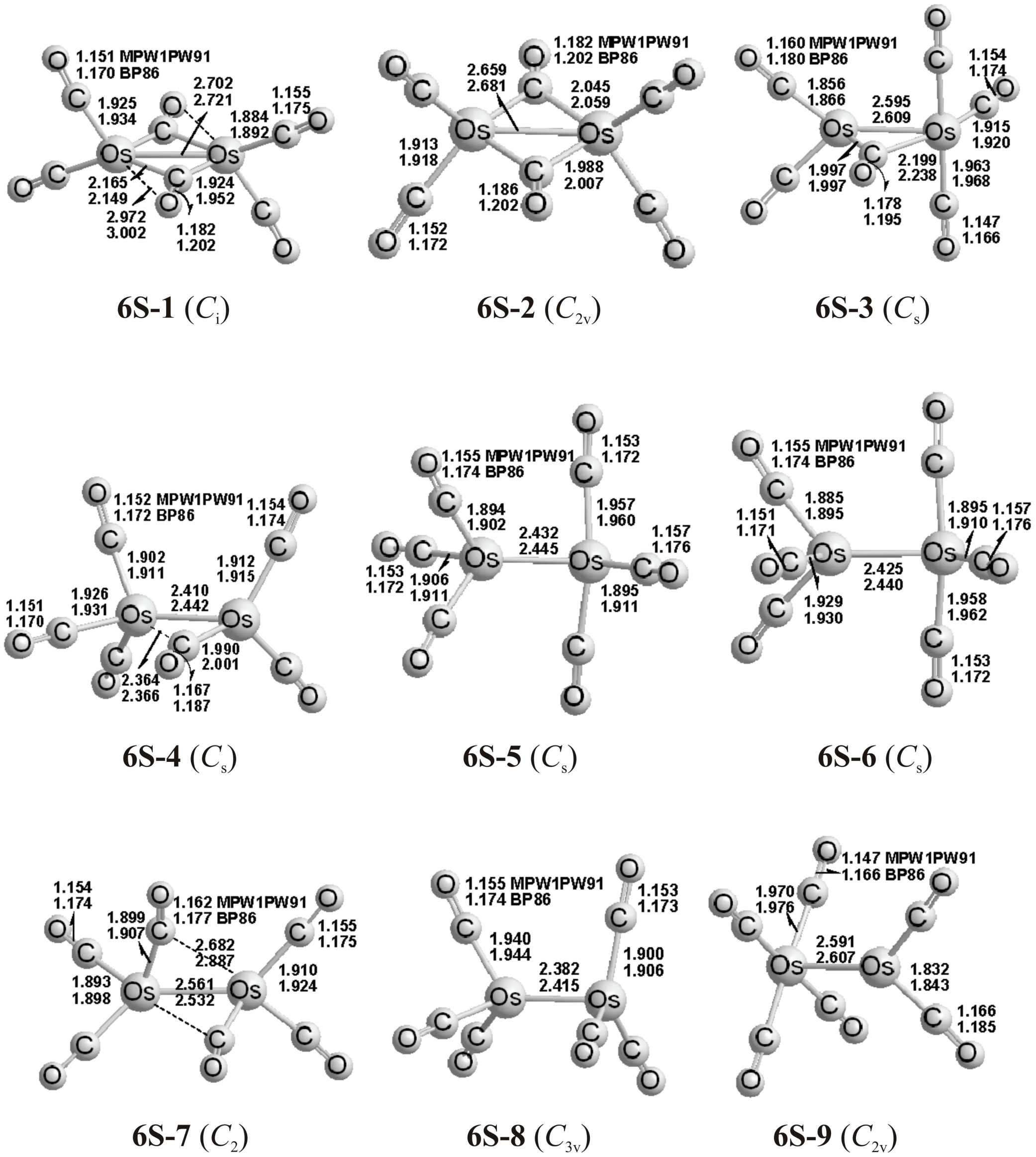
Structure **7S-4** of $Os_2(CO)_7$ (Figure 1, Table 1) is closely related to **7S-2** by rotation around the Os≡Os triple bond. A small imaginary vibrational frequency of 44i (MPW1PW91) or 50i (BP86) suggests that **7S-4** is a transition state rather than a genuine minimum. Following the normal mode corresponding to this imaginary vibrational frequency of **7S-4** leads to **7S-2**. Structure **7S-4** is predicted to lie in energy above **7S-2** by 2.0 kcal mol^{-1} (MPW1PW91) or 2.4 kcal mol^{-1} (BP86). This low rotation barrier about the Os≡Os triple bond in **7S-2** with **7S-4** as a transition state is consistent with the cylindrical symmetry of a typical ($\sigma + 2\pi$) Os≡Os triple bond in **7S-2** analogous to the C≡C triple bond in acetylene.

Structures **7S-6** (C_2) and **7S-9** (C_{2v}) are two triply bridged singlet structures of $Os_2(CO)_7$ (Figure 1, Table 2). For **7S-6** the BP86 functional predicts a rather small imaginary vibrational frequency at 12i cm^{-1}, which is removed by the finer integration grid (120, 974). In contrast, the MPW1PW91 functional predicts a larger imaginary vibrational frequency for **7S-6** at 111i cm^{-1}. Following the corresponding normal mode leads to a C_1 structure **7S-5,** in which two of the three bridging CO groups in **7S-6** become a semibridging CO group and a terminal CO group. The MPW1PW91 structure **7S-5** is predicted to lie within ≈1 kcal mol^{-1} of **7S-4** and 4.0 kcal mol^{-1} below **7S-6**. The Os−Os bond distance of **7S-5** is predicted to be ≈0.1 Å longer than that of **7S-6**. Structure **7S-9** (C_{2v}) is predicted to have a small imaginary vibrational frequency at 56i cm^{-1}, which is a genuine imaginary vibrational frequency, since it changes trivially to 57i cm^{-1} when a finer integration grid (120, 974) is used. Following the corresponding normal mode leads to **7S-6**. The predicted energies for these two structures above the global minimum structure **7S-1** are 10.0 kcal mol^{-1} (MPW1PW91) or 8.3 kcal mol^{-1} for **7S-6** and 20.5 kcal mol^{-1} (MPW1PW91) or 18.2 kcal mol^{-1} for **7S-9**.

Two singlet structures **7S-7** (C_2) and **7S-8** (C_{2v}) for $Os_2(CO)_7$ were found consisting of two $Os(CO)_3$ units bridged by a carbonyl group (Figure 1, Table 2). The Os≡Os bond lengths in these two structures fall in the range of a triple bond thereby giving both osmium atoms the favored 18-electron configuration. Structure **7S-7** is predicted to have an imaginary vibrational frequency at 69i cm^{-1}. Following the corresponding normal mode leads to a C_1 structure, and finally to **7S-2** (C_s). Structure **7S-8** (C_{2v}), is predicted to have an imaginary vibrational frequency at 23i cm^{-1}. Following the corresponding normal mode leads first to **7S-7** and finally also to **7S-2.** The energies above the global minimum **7S-1** of these two structures are predicted to be 11.3 kcal mol^{-1} (MPW1PW91) or 13.0 kcal mol^{-1} (BP86) for **7S-7** and 12.0 kcal mol^{-1} (MPW1PW91) or 13.5 kcal mol^{-1} (BP86) for **7S-8.**

$Os_2(CO)_6$

Nine singlet and six triplet structures of $Os_2(CO)_6$ were found in this work (Figures 2 and 3 and Tables 4, 5, and 7). The predicted lowest energy $Os_2(CO)_6$ structures are two doubly bridged singlets **6S-1** (C_i) and **6S-2** (C_{2v}) of nearly identical energies. Both structures are genuine minima with all real vibrational frequencies (Table 4). Structures **6S-1** and **6S-2** (Figure 2) may be obtained by removal of a different terminal carbonyl group from structure **7S-1** (Figure 1). The Os=Os bond lengths of 2.702 Å (MPW1PW91) or 2.721 Å (BP86) for **6S-1** and



6S-1 (C_i) **6S-2** (C_{2v}) **6S-3** (C_s)

6S-4 (C_s) **6S-5** (C_s) **6S-6** (C_s)

6S-7 (C_2) **6S-8** (C_{3v}) **6S-9** (C_{2v})

Figure 2. The nine optimized singlet structures of $Os_2(CO)_6$.

2.659 Å (MPW1PW91) or 2.681 Å (BP86) for **6S-2** can be interpreted as formal double bonds giving both osmium atoms 16-electron configurations. The bridging carbonyl groups in **6S-1** are predicted to exhibit a single infrared-active bridging ν(CO) frequency at 1795 cm^{-1} (BP86) as well as an infrared inactive frequency at 1801 cm^{-1}. However, the bridging carbonyl groups in **6S-2** are predicted to exhibit a pair of infrared active bridging ν(CO) frequencies at 1781 and 1805 cm^{-1} (Table 6).

The unsymmetrical bridging singlet $Os_2(CO)_6$ structure **6S-3** (Figure 2, Table 4) may be obtained by removal of one terminal CO group from the $Os_2(CO)_7$ structure **7S-3** (Figure 1). Structure **6S-3** is predicted to lie in energy 1.3 kcal mol^{-1} (MPW1PW91) or 6.1 kcal mol^{-1} (BP86) above **6S-1.** Structure **6S-3** has a very small imaginary vibrational frequency at 13*i* cm^{-1} (BP86), which may be arise from numerical integration errors. The Os≡Os bond distance in **6S-3** is predicted to be 2.595 Å (MPW1PW91) or 2.609 Å (BP86), suggesting a formal triple bond to give the osmium atom bearing two terminal CO groups a 16-electron configuration and the osmium atom bearing three terminal CO groups the favored 18-electron configuration. The unsymmetrical bridging CO group in **6S-3** is predicted (BP86) to exhibit a single ν(CO) frequency at 1839 cm^{-1}, which is appreciably higher than the bridging ν(CO) frequencies in **6S-1** and **6S-2** (Table 6).

A semibridging carbonyl structure **6S-4** (Figure 2, Table 4) is also found to be a genuine minimum, lying in energy above the global minimum structure **6S-1** by

Table 3. Infrared active ν(CO) vibrational frequencies / cm^{-1} predicted for $Os_2(CO)_7$. Infrared intensities given in parentheses are expressed in km mol^{-1}, bridging ν(CO) frequencies are printed in bold type

	BP86
7S-1 (C_s)	**1799(408), 1827(455),** 1968(717), 2002(1187), 2010(1241), 2016(1011), 2070(441)
7S-2 (C_s)	1954(255), 1965(415), 1973(1226), 1985(1506), 1989(485), 2023(1621), 2056(28)
7S-3 (C_s)	**1847(518),** 1952(419), 1990(1613), 1997(585), 2009(886), 2012(1094), 2068(244)
7S-4 (C_s)	1950(278), 1973(3), 1978(1735), 1982(158), 1987(1758), 2026(1561), 2057(18)
7S-5 (C_2)$^{(a)}$	**1952(590)**, **2021(750),** 2094(863), 2114(1238), 2124(1734), 2142(1694), 2205(159)
7S-6 (C_2)	**1873(719), 1874(197), 1888(765),** 1991(737), 1992(773), 2021(2620)
7S-7 (C_2)	**1868(519),** 1976(460), 1988(1414), 1989(1370), 2024(1724), 2054(51)
7S-8 (C_{2v})	**1866(468),** 1978(83), 1990(1785), 1991(1402), 2026(1683), 2056(56)
7S-9 (C_{2v})	**1878(737), 1899(746)**, **1902(408),** 1985(1431), 2013(2747)

(a) Since this structure was only obtained with the MPW1PW91 method, the ν(CO) frequencies necessarily were also obtained by this method. In our experience ν(CO) frequencies obtained by the MPW1PW91 method are ≈100 cm^{-1} higher than those obtained by the BP86 method.

Table 4. Total energies (E / hartree), relative energies (ΔE / kcal mol^{-1}), number of imaginary vibrational frequencies (Nimag), and Os-Os bond distances / Å of the four bridged singlet structures of $Os_2(CO)_6$

		6S-1 (C_i)	**6S-2** (C_{2v})	**6S-3** (C_s)	**6S-4** (C_s)
MPW1PW91	E	−861.56344	−861.56144	−861.56144	−861.55924
	ΔE	0	1.3	1.3	2.6
	Nimag	0	0	0	0
	Os-Os	2.702	2.659	2.595	2.410
BP86	E	−862.01102	−862.01208	−862.00136	−862.00591
	ΔE	0	−0.7	6.1	3.2
	Nimag	0	0	1 (13i)	0
	Os-Os	2.721	2.681	2.609	2.442

Table 5. Total energies (E / hartree), relative energies (ΔE / kcal mol^{-1}), number of imaginary vibrational frequencies (Nimag), and Os-Os bond distances / Å for the five singlet structures of $Os_2(CO)_6$ without bridging carbonyl groups

		6S-5 (C_s)	**6S-6** (C_s)	**6S-7** (C_2)	**6S-8** (C_{3v})	**6S-9** (C_{2v})
MPW1PW91	E	−861.55639	−861.55545	−861.55025	−861.54976	−861.54004
	ΔE	4.4	5.0	8.3	8.9	14.7
	Nimag	1 (26i)	1 (46i)	1 (30i)	2 (83i, 83i)	0
	Os-Os	2.432	2.425	2.561	2.382	2.591
BP86	E	−862.00096	−861.99943	−861.99536	−861.99609	−861.98152
	ΔE	6.3	7.3	9.8	9.4	18.5
	Nimag	1 (24i)	1 (56i)	1 (25i)	2 (81i, 81i)	0
	Os-Os	2.445	2.440	2.532	2.415	2.607

Table 6. Infrared active ν(CO) vibrational frequencies / cm^{-1} predicted for $Os_2(CO)_6$. Infrared intensities given in parentheses are expressed in km mol^{-1}, bridging ν(CO) frequencies are printed in bold type

	BP86
6S-1 (C_i)	**1795(903),** 1972(1894), 2005(2198)
6S-2 (C_{2v})	**1781(613), 1805(373),** 1976(1965), 2001(1852), 2033(116)
6S-3 (C_s)	**1839(613),** 1946(639), 1986(1048), 1998(1631), 2004(881), 2071(184)
6S-4 (C_s)	**1877(641)**, 1953(544), 1986(791), 1986(1448), 2002(1328), 2055(312)
6S-5 (C_s)	1955(476), 1956(213), 1973(1948), 1977(1371), 2009(1078), 2049(132)
6S-6 (C_s)	1953(319), 1957(279), 1977(1857), 1979(1472), 2009(939), 2051(168)
6S-7 (C_2)	1946(344), 1952(185), 1958(2020), 1968(1277), 1999(2007)
6S-8 (C_{3v})	1953(533), 1978(1457), 2004(895), 2053(243)
6S-9 (C_{2v})	1925(754), 1975(1593), 2002(1325), 2003(1412), 2089(254)
6T-1 (C_2)	**1810(981),** 1959(434), 1968(1478), 1987(2284), 2024(132)
6T-2 (C_{2v})	1937(420), 1980(1821), 1982(1456), 2002(807), 2072(135)
6T-3 (C_i)	**1808(961),** 1959(2225), 1986(2220)
6T-4 (C_s)	**1824(567),** 1943(280), 1955(1112), 1961(1430), 1981(1471), 2020(311)
6T-5 (C_s)	1942(174), 1954(187), 1963(2063), 1973(1391), 1977(1515), 2039(68)
6T-6 (C_s)	1928(910), 1951(470), 1966(1464), 1971(1192), 1992(1266), 2038(195)

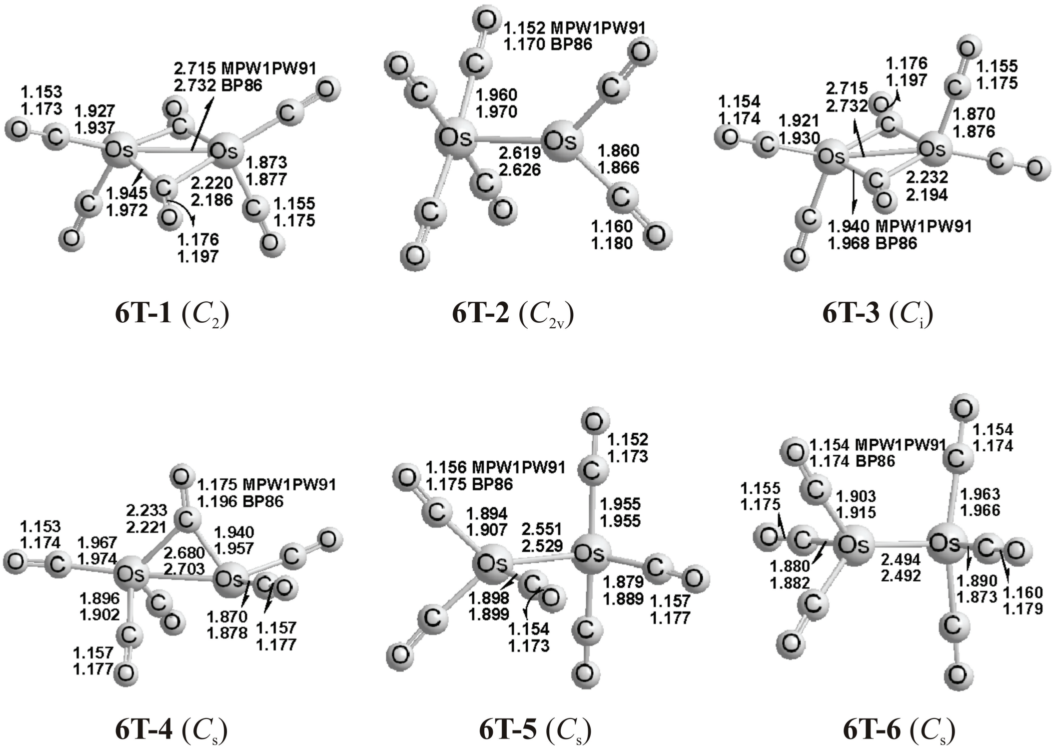
only 2.6 kcal mol^{-1} (MPW1PW91) or 3.2 kcal mol^{-1} (BP86). The Os≣Os distance is predicted to be 2.410 Å (MPW1PW91) or 2.442 Å (BP86), suggesting the quadruple bond required to give both osmium atoms the favored 18-electron configuration. The semibridging CO group in **6S-4** is predicted to exhibit a ν(CO) frequency at 1877 cm^{-1} (Table 6).

A number of somewhat higher energy structures without bridging carbonyl groups were also found for $Os_2(CO)_6$ (Figure 2 and Table 5). The structures **6S-5** and **6S-6** (Figure 2 and Table 5) are predicted to be almost degenerate in energy, lying at 4.4 kcal mol^{-1} (MPW1PW91) or 6.3 kcal mol^{-1} (BP86) (**6S-5**) and 5.0 kcal mol^{-1} (MPW1PW91) or 7.3 kcal mol^{-1} (BP86) (**6S-6**) above the global minimum **6S-1.** Following the normal mode corresponding to the small imaginary vibrational frequencies of **6S-5** and **6S-6** (Table 5) leads first to a C_1 structure and finally to structure **6S-4** (C_s). The very short Os≣Os bond distances in **6S-5** and **6S-6** fall in the 2.42 Å to 2.44 Å range consistent with the quadruple bond required to give both osmium atoms the favored 18-electron configuration.

Another pair of degenerate structures are **6S-7** (C_2) and **6S-8** (C_{3v}) (Figure 2 and Table 5). Structure **6S-7**(C_2), at 8.3 kcal mol^{-1} (MPW1PW91) or 9.8 kcal mol^{-1} (BP86) above the global minimum **6S-1**, is an unbridged structure with a small imaginary vibrational frequency at 25*i* cm^{-1} (BP86), which increases trivially to 26*i* cm^{-1} when a finer integration grid (120, 974) is used. Following the corresponding normal mode leads first to a C_1 structure and finally to the bridged structure **6S-3.** The predicted Os-Os distance is 2.561 Å (MPW1PW91) or 2.532 Å (BP86), which is somewhat long for the formal quadruple bond required to give both osmium atoms the favored 18-electron configuration.

The C_{3v} structure **6S-8** (Figure 2), which is essentially degenerate with **6S-7**, can be derived from an eclipsed D_{3h} unbridged structure of $Os_2(CO)_6$ (not shown) by following the normal mode corresponding to the 184*i* cm^{-1} imaginary vibrational frequency of the latter structure. Following the normal mode corresponding to the two imaginary vibrational frequencies of **6S-8** at 81*i* cm^{-1} (BP86) then leads to **6S-4**. The Os≣Os distance in **6S-8** of 2.382 Å (MPW1PW91) or 2.415 Å (BP86) is the shortest found in any of the predicted $Os_2(CO)_6$ structures and is consistent with the formal quadruple bond needed to give both osmium atoms the favored 18-electron configuration.

An unsymmetrical C_{2v} $(OC)_4Os{\equiv}Os(CO)_2$ structure **6S-9** is the only genuine minimum found for unbridged structures of $Os_2(CO)_6$ (Figure 2, Table 5). Structure **6S-9** is predicted to lie in energy above **6S-1** by 14.7 kcal mol^{-1} (MPW1PW91) or 18.5 kcal mol^{-1} (BP86) with an Os≡Os distance of 2.591 Å (MPW1PW91) or 2.607 Å (BP86), corresponding to a



6T-1 (C_2) **6T-2** (C_{2v}) **6T-3** (C_i)

6T-4 (C_s) **6T-5** (C_s) **6T-6** (C_s)

Figure 3. The six optimized triplet structures of $Os_2(CO)_6$.

formal triple bond giving one of the osmium atoms the favored 18-electron configuration but the other osmium atom only a 16-electron configuration.

Six triplet structures of $Os_2(CO)_6$ (Figure 3 and Table 7) were found within 25 kcal mol^{-1} of the global minimum **6S-1**. The doubly bridged structures **6T-1** (C_2) and **6T-3** (C_i) have a *cis-trans* relationship and both have all real vibrational frequencies. Structure **6T-1** is predicted to be the lowest energy triplet structure, lying in energy above the global minimum **6S-1** by 13.6 kcal mol^{-1} (MPW1PW91) or 15.0 kcal mol^{-1} (BP86). Struc-

Table 7. Total energies (E / hartree), energies relative to **6S-1** (ΔE / kcal mol^{-1}), number of imaginary vibrational frequencies (Nimag), Os-Os bond distances / Å, and spin contamination $\langle S^2 \rangle$ of the triplet structures of $Os_2(CO)_6$

	6T-1 (C_2)	**6T-2** (C_{2v})	**6T-3** (C_i)	**6T-4** (C_s)	**6T-5** (C_s)	**6T-6** (C_s)
MPW1PW91						
E	−861.54178	−861.54180	−861.53728	−861.53435	−861.53036	−861.52963
ΔE	13.6	13.6	16.4	18.3	20.8	21.2
Nimag	0	0	1 (9*i*)	1 (17*i*)	1 (12*i*)	0
Os-Os	2.715	2.619	2.715	2.680	2.551	2.494
$\langle S^2 \rangle$	2.03	2.01	2.04	2.01	2.02	2.02
BP86						
E	−861.98715	−861.96793	−861.98402	−861.97478	−861.97078	−861.97127
ΔE	15.0	27.0	16.9	22.7	25.2	24.9
Nimag	0	1 (1*i*)	0	1 (39*i*)	1 (5*i*)	0
Os-Os	2.732	2.626	2.732	2.703	2.529	2.492
$\langle S^2 \rangle$	2.01	2.01	2.01	2.00	2.00	2.00

ture **6T-3** lies 2.8 kcal mol^{-1} (MPW1PW91) or 1.9 kcal mol^{-1} (BP86) in energy above **6T-1**. The bridging carbonyl groups are predicted (BP86) to exhibit an infrared active ν(CO) frequency of 1810 cm^{-1} in **6T-1** and at 1808 cm^{-1} in **6T-3** (Table 6) as well as infrared inactive frequencies at 1818 cm^{-1} for both **6T-1** and **6T-3.** The Os=Os bond distances in **6T-1** and **6T-3** fall in the narrow range 2.71 Å to 2.73 Å corresponding to formal double bonds. The most likely interpretation of the bonding in structures **6T-1** and **6T-3** has the two unpaired electrons in a ($\sigma + {}^{2}\!/_{2}$) π Os=Os double bond with a 16-electron configuration for each osmium atom.

Structure **6T-2** (Figure 3 and Table 7) is an unsymmetrical unbridged triplet structure consisting of one Os(CO)$_4$ unit and one Os(CO)$_2$ unit connected by an Os≡Os triple bond as suggested by the predicted Os≡Os distance of 2.619 Å (MPW1PW91) or 2.626 Å (BP86). Structure **6T-2** is predicted to lie in energy above **6S-1** by 13.6 kcal mol^{-1} (MPW1PW91) or 27.0 kcal mol^{-1} (BP86).

Structure **6T-4** (C_s) is the only triplet structure of Os$_2$(CO)$_6$ found to have a single bridging CO group (Figure 3 and Table 7). It is predicted to lie in energy above **6S-1** by 18.3 kcal mol^{-1} (MPW1PW91) or 22.7 kcal mol^{-1} (BP86) with a small imaginary vibrational frequency at 39*i* cm^{-1} (BP86), which changes insignificantly to 38*i* cm^{-1} when a finer integration grid (120, 974) is used. Following the corresponding normal mode leads first to a C_1 structure and finally to the **6T-3** (C_i) doubly bridging structure**.** The bridging CO group in **6T-4** is predicted (BP86) to exhibit a single ν(CO) frequency at 1824 cm^{-1} (Table 6).

The two unbridged triplet Os$_2$(CO)$_6$ structures **6T-5** (C_s) and **6T-6** (C_s) (Figure 3, Table 7) are *cis* and *trans* isomers, respectively, lying in energy within 0.4 kcal mol^{-1} of each other and 21 kcal mol^{-1} (MPW1PW91) or 25 kcal mol^{-1} (BP86) above the global minimum **6S-1**. The Os≡Os distances in the two structures are in the 2.49 Å to 2.55 Å range for a formal triple bond, thereby giving both osmium atoms the 17-electron configurations required for triplet spin multiplicity. The *cis* structure **6T-5** is predicted to have a negligible imaginary vibrational frequency at 5*i* cm^{-1} (BP86), which may arise from numerical integration errors. The *trans* structure **6T-5** is found to be a genuine minimum with all real vibrational frequencies.

Dissociation Energies

Table 8 summarizes the energies of the two possible dissociation pathways of Os$_2$(CO)$_7$. The energies for the carbonyl dissociation reaction **7S-1** (C_s) → **6S-1** (C_i) + CO are lower than the energies of the dimer fragmentation reaction **7S-1** (C_s) → Os(CO)$_4$ + Os(CO)$_3$ by 8.3 kcal mol^{-1} (MPW1PW91) or 9.8 kcal mol^{-1} (BP86)

Table 8. Dissociation energies expressed in kcal mol^{-1} for Os$_2$(CO)$_7$

	MPW1PW91	BP86
7S-1 (C_s) → **6S-1** (C_i) + CO	43.6	43.3
7S-3 (C_s) → **6S-3** (C_s) + CO	40.7	38.8
7S-1 (C_s) → Os(CO)$_4$ + Os(CO)$_3$	51.9	53.1

Table 9. Correlation of Os-Os bond lengths (MPW1PW91) with formal bond order in binary osmium carbonyls presumed to have the favored 18-electron configuration

Compound	Structure	Os-Os length / Å	Formal bond order
Os$_3$(CO)$_{12}$	Expt.[5]	2.88	1
Os$_4$(CO)$_{16}$	Expt.[6,7]	3.01 to 3.05	1
Os$_2$(CO)$_8$(μ-CO)	**9S-2**[17]	2.91	1
(OC)$_5$Os→Os(CO)$_4$	**9S-4**[17]	2.94	1
Os$_2$(CO)$_8$	**8S-2**[17]	2.72	2
Os$_2$(CO)$_6$(μ-CO)$_2$	**8S-4**[17]	2.86	2
Os$_2$(CO)$_7$	**7S-2**	2.54	3
Os$_2$(CO)$_6$(μ-CO)	**7S-7**	2.50	3
Os$_2$(CO)$_6$	**6S-4**	2.41	4

suggesting preference for CO dissociation over rupture of the osmium-osmium bond in $Os_2(CO)_7$.

DISCUSSION

A structural feature that is completely absent in the 24 structures for the highly unsaturated $Os_2(CO)_7$ and $Os_2(CO)_6$ obtained in these DFT studies is a four-electron donor bridging η^2-μ-CO carbonyl group. Such a special carbonyl group is recognized by an unusually low ν(CO) frequency as well as a short metal-oxygen distance, typically 2.0 to 2.3 Å, consistent with involvement of the carbonyl oxygen as well as the carbonyl carbon in the metal-ligand bonding. In striking contrast, several low energy binuclear rhenium carbonyl derivatives, including $Re_2(CO)_9$, were found by DFT methods[41] to have low energy structures containing such four-electron donor η^2-μ-CO groups. The absence of four-electron donor η^2-μ-CO groups in unsaturated osmium carbonyl chemistry relates to the decreasing oxophilicity in going to the right in a transition metal series. On this basis osmium is expected to be less oxophilic than rhenium.

Since four-electron donor bridging η^2-μ-CO carbonyl groups appear to be avoided in osmium carbonyl chemistry, the unsaturation in $Os_2(CO)_7$ and $Os_2(CO)_6$ can only be accommodated by multiple osmium-osmium bonding and/or osmium valence electron configurations less than the favored 18 electrons. In order to assess the formal osmium-osmium bond order in these unsaturated derivatives, we have analyzed the relationship between osmium-osmium distances and formal bond orders in derivatives where the osmium atoms are most likely to have the favored 18-electron configurations (Table 9). In Table 9 the experimental osmium-osmium distances are given for $Os_3(CO)_{12}$ and $Os_4(CO)_{16}$, which have been characterized by X-ray diffraction.[5,6,7] The other information on osmium-osmium distances in Table 9 is taken from this and previous[17] DFT studies using the MPW1PW91 method. From this information the lengths of osmium-osmium bonds in osmium carbonyl derivatives are seen to be 2.9 Å to 3.0 Å, 2.7 Å to 2.8 Å, 2.5 Å, and 2.4 Å for formal single, double, triple, and quadruple bonds, respectively. This information is used as a rough guideline for the assignment of formal osmium-osmium bond orders in the other $Os_2(CO)_n$ derivatives discussed in this paper where one or both osmium atoms may have less than the favored 18-electron configuration.

The global minimum structure of $Os_2(CO)_7$, namely **7S-1** (Figure 1) with two bridging carbonyl groups and an Os=Os distance of 2.671 Å (MPW1PW91), suggesting a formal double bond, does not have a counterpart in any of the structures for $Fe_2(CO)_7$ found in our previous DFT studies.[40] However, the next higher lying $Os_2(CO)_7$ structure, namely **7S-2** with no bridging carbonyl groups and an Os≡Os distance of 2.537 Å suggesting a formal Os≡Os triple bond, is very similar to the global minimum found for $Fe_2(CO)_7$ except that in this $Fe_2(CO)_7$ structure, two of the seven carbonyl groups are slightly semi-bridging.

The global minimum structure of $Os_2(CO)_6$, namely **6S-1** (Figure 2), can be derived from that of $Os_2(CO)_7$ (**7S-1** in Figure 1) by removal of a carbonyl group from the $Os(CO)_3$ unit. Thus **6S-1** retains the formal Os=Os double bond at 2.702 Å as well as the two bridging carbonyl groups. However, now both osmium atoms have 16-electron configurations. Slightly higher energy $Os_2(CO)_6$ structures, such as **6S-4**, have short Os≣Os distances around 2.4 Å, consistent with the formal quadruple bonds necessary to give both osmium atoms the favored 18-electron configuration. Low energy structures of $Fe_2(CO)_6$ related to both **6S-1** and **6S-4** were found in our previous DFT study.[40]

Supplementary Materials. – Supporting informations to the paper are enclosed to the electronic version of the article. Tables S1-S7: Theoretical harmonic vibrational frequencies for $Os_2(CO)_7$ (13 isomers), $Os_2(CO)_6$ (15 isomers) using the BP86 method; Tables S8-S35: Theoretical Cartesian coordinates for $Os_2(CO)_7$ (13 isomers), $Os_2(CO)_6$ (15 isomers) using the MPW1PW91 method; Complete Gaussian 03 reference (Reference 38). These data can be found on the website of *Croatica Chemica Acta* (http://public.carnet.hr/ccacaa).

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SAŽETAK

Heptakarbonildiosmij i heksakarbonildiosmij: Dva jako nezasićena binuklearna osmijeva karbonila

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Pomoću DFT računa pronađeno je devet singletnih struktura za $Os_2(CO)_7$ i 15 struktura (devet singleta i šest tripleta) za $Os_2(CO)_6$ što ukazuje na vrlo kompleksne plohe potencijalne energije. Globalni minimum za $Os_2(CO)_7$ je karbonilnom skupinom dvostruko premoštena struktura $Os_2(CO)_5(\mu\text{-}CO)_2$ s Os=Os vezom od 2.67 Å što indicira formalnu dvostruku vezu i 16-elektronsku, prije nego 18-elektronsku konfiguraciju za jedan od atoma osmija. Ipak, na neznatno višoj energiji (3.2 kcal mol^{-1}) nalazi se nepremoštena $Os_2(CO)_7$ struktura s kraćom Os≡Os vezom od 2.54 Å, koja odgovara formalno trostrukoj vezi i 18-elektronskoj konfiguraciji za svaki atom osmija. Globalni minimum za $Os_2(CO)_6$ može se postići polazeći od $Os_2(CO)_7$ uklanjanjem jedne karbonilne grupe, zadržavajući Os=Os dvostruku vezu i dvije premošćujuće karbonilne skupine. Energetski nešto viša struktura $Os_2(CO)_6$, koja leži na oko 3 kcal mol^{-1} ili nešto više iznad globalnog minimum, ima kraće osmij-osmij udaljenosti od oko 2.4 Å, što je u skladu s formalnom četverostrukom vezom potrebnom da oba osmijeva atoma imaju favoriziranu 18-elektronsku konfiguraciju. Niti jedna od 24 strukture za $Os_2(CO)_7$ i $Os_2(CO)_6$, pronađene u ovom radu, ne posjeduje premošćujuću četiri-elektronsku donorsku η^2-μ-CO karbonilnu skupinu.