

Homoleptic Mononuclear and Binuclear Osmium Carbonyls $\text{Os}(\text{CO})_n$ ($n = 3-5$) and $\text{Os}_2(\text{CO})_n$ ($n = 8, 9$): Comparison with the Iron Analogues

Bing Xu,[†] Qian-Shu Li,^{*,†,‡} Yaoming Xie,[§] R. Bruce King,^{*,†,§} and Henry F. Schaefer III[§]

Institute of Chemical Physics, Beijing Institute of Technology, Beijing 100081, China, Center for Computational Quantum Chemistry, South China Normal University, Guangzhou 510631 China, and Department of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

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The structures and energetics of the experimentally known $\text{Os}(\text{CO})_n$ ($n = 3-5$), $\text{Os}_2(\text{CO})_9$, and $\text{Os}_2(\text{CO})_8$ have been investigated using density functional theory. For $\text{Os}(\text{CO})_5$, the lowest-energy structure is the singlet D_{3h} trigonal bipyramid. However, the C_{4v} square pyramid for $\text{Os}(\text{CO})_5$ lies only ~ 1.5 kcal/mol higher in energy, suggesting extraordinary fluxionality. For the coordinatively unsaturated $\text{Os}(\text{CO})_4$ and $\text{Os}(\text{CO})_3$, a D_{2d} strongly distorted tetrahedral structure and a C_s bent T-shaped structure are the lowest-energy structures, respectively. For $\text{Os}_2(\text{CO})_9$, the experimentally observed singly bridged $\text{Os}_2(\text{CO})_8(\mu\text{-CO})$ structure is the lowest-energy structure. A triply bridged $\text{Os}_2(\text{CO})_6(\mu\text{-CO})_3$ structure analogous to the known $\text{Fe}_2(\text{CO})_9$ structure is a transition state rather than a true minimum and collapses to the singly bridged global minimum structure upon following the corresponding normal mode. An unbridged $(\text{OC})_5\text{Os} \rightarrow \text{Os}(\text{CO})_4$ structure with a formal $\text{Os} \rightarrow \text{Os}$ dative bond analogous to known stable complexes of the type $(\text{R}_3\text{P})_2(\text{OC})_3\text{Os} \rightarrow \text{W}(\text{CO})_5$ is also found for $\text{Os}_2(\text{CO})_9$ within 8 kcal/mol of the global minimum. The global minimum for the coordinatively unsaturated $\text{Os}_2(\text{CO})_8$ is a singly bridged $(\text{OC})_4\text{Os}(\mu\text{-CO})\text{Os}(\text{CO})_3$ structure derived from the $\text{Os}_2(\text{CO})_9$ global minimum by loss of a terminal carbonyl group. However, the unbridged structure for $\text{Os}_2(\text{CO})_8$ observed in low-temperature matrix experiments lies only ~ 1 kcal/mol above this global minimum. In all cases, the triplet structures for these osmium carbonyls have significantly higher energies than the corresponding singlet structures.

1. Introduction

Osmium carbonyl chemistry dates back to 1943 when Hieber and Stallmann¹ first synthesized $\text{Os}(\text{CO})_5$ as a rather unstable liquid by the carbonylation of OsO_4 or osmium halides at elevated pressures. For more than 20 years after this discovery, very little work was done with $\text{Os}(\text{CO})_5$, presumably because of its instability and the high cost of osmium. Subsequently, in 1967 Calderazzo and L'Epplattienier² proposed the expected trigonal-bipyramidal D_{3h} structure for $\text{Os}(\text{CO})_5$ based on its infrared (IR) spectrum.

Hieber and Stallmann in their original work¹ also isolated a second binary osmium carbonyl as a yellow solid, either from the decomposition of $\text{Os}(\text{CO})_5$ or from the original carbonylation reaction mixture. They assumed that this solid osmium carbonyl was $\text{Os}_2(\text{CO})_9$ by analogy with the corresponding iron carbonyl system, where $\text{Fe}(\text{CO})_5$ has been known for more than a century³ to decompose photochemically to $\text{Fe}_2(\text{CO})_9$.

Following the original work by Hieber and Stallmann,¹ osmium carbonyl chemistry apparently lay dormant for approximately 18 years until Corey and Dahl⁴ repeated the carbonylation of OsO_4 to obtain the yellow crystals believed by Hieber and Stallmann¹ to be $\text{Os}_2(\text{CO})_9$. However, Corey and Dahl found by X-ray crystallography that this yellow

* To whom correspondence should be addressed. E-mail: qsl@scnu.edu.cn (Q.-S.L.), rbking@chem.uga.edu (R.B.K.).

[†] Beijing Institute of Technology.

[‡] South China Normal University.

[§] University of Georgia.

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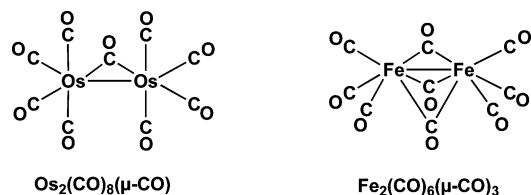


Figure 1. Comparison of the structures of $\text{Os}_2(\text{CO})_9$ and $\text{Fe}_2(\text{CO})_9$.

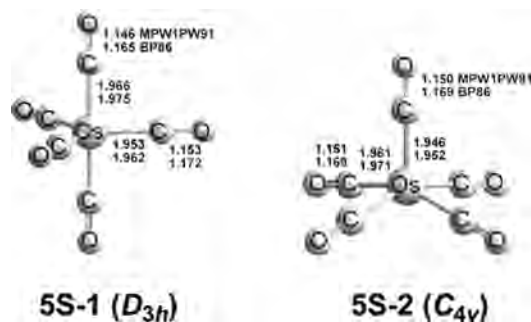


Figure 2. Two energetically low-lying structures for $\text{Os}(\text{CO})_5$.

solid is actually $\text{Os}_3(\text{CO})_{12}$, an apparent analogue of the long-known^{5,6} iron carbonyl $\text{Fe}_3(\text{CO})_{12}$ but with a different structure having all terminal carbonyl groups.

The genuine $\text{Os}_2(\text{CO})_9$ was finally prepared in 1970 by Moss and Graham^{7,8} via photolysis of $\text{Os}(\text{CO})_5$ in a heptane solution. Because of the instability of $\text{Os}_2(\text{CO})_9$, the temperature needs to be kept below -40°C to prevent conversion to the much more stable $\text{Os}_3(\text{CO})_{12}$. The instability of $\text{Os}_2(\text{CO})_9$ has so far prevented determination of its structure by definitive X-ray diffraction methods. However, interpretation of the IR spectrum of $\text{Os}_2(\text{CO})_9$ in the $\nu(\text{CO})$ region^{7,8} implicates a structure $\text{Os}_2(\text{CO})_8(\mu\text{-CO})$ with a single bridging carbonyl group rather than a structure $\text{Os}_2(\text{CO})_6(\mu\text{-CO})_3$ analogous to that of $\text{Fe}_2(\text{CO})_9$ ^{9,10} with three bridging carbonyl groups (Figure 1).

Coordinatively unsaturated osmium carbonyls have been generated by photolysis of stable osmium carbonyl derivatives and characterized by their $\nu(\text{CO})$ frequencies. Bogdan and Weitz¹¹ have shown that photolysis of $\text{Os}(\text{CO})_5$ in the gas phase generates $\text{Os}(\text{CO})_4$, $\text{Os}(\text{CO})_3$, and $\text{Os}_2(\text{CO})_8$. The photolysis can be made to generate $\text{Os}_2(\text{CO})_8$ selectively by using a binuclear osmium carbonyl precursor^{12,13} such as $\text{Os}_2(\text{CO})_9$ or $\text{Os}_2(\text{CO})_8(\text{C}_2\text{H}_4)$. The IR $\nu(\text{CO})$ frequencies of $\text{Os}_2(\text{CO})_8$ generated in this manner indicate the absence of bridging carbonyl groups. They suggest a structure derived from that of $\text{Os}_2(\text{CO})_9$ (Figure 1) by removal of its single bridging carbonyl group.

Table 1. Total Energies (E , in hartree) and Relative Energies (ΔE , in kcal/mol) of $\text{Os}(\text{CO})_5^a$

		5S-1 (D_{3h})	5S-2 (C_{4v})
MPW1PW91	E	-657.47752	-657.47519
	ΔE	0	1.5
	Nimag	0	1 (35i)
BP86	E	-657.76410	-657.76190
	ΔE	0	1.4
	Nimag	0	1 (33i)

^a The number of imaginary vibrational frequencies (Nimag) is also listed.

Zhou and Andrews¹⁴ have also generated unsaturated mononuclear osmium carbonyls $\text{Os}(\text{CO})_n$ ($n = 1-4$) by the reaction of laser-ablated Os atoms with carbon monoxide during condensation in a neon matrix. Comparison of the observed $\nu(\text{CO})$ spectra in the low-temperature matrix with the $\nu(\text{CO})$ frequencies calculated by density functional theory (DFT) indicates $\text{Os}(\text{CO})_4$ to have a singlet ground state with distorted tetrahedral D_{2d} symmetry in accordance with the earlier suggestion of Bogdan and Weitz.¹¹ This is distinctly different from the square-planar D_{4h} structure that might be naively expected by analogy of the d^8 $\text{Os}(0)$ in $\text{Os}(\text{CO})_4$ with the isoelectronic Ir(I) and Pt(II), which form numerous square-planar complexes.

Previous research systematically used DFT to study the trinuclear osmium carbonyls $\text{Os}_3(\text{CO})_n$ ($n = 9-12$)¹⁵ and the tetranuclear osmium carbonyls $\text{Os}_4(\text{CO})_n$ ($n = 12-16$).¹⁶ This paper extends these studies to the mononuclear osmium carbonyls $\text{Os}(\text{CO})_n$ ($n = 3-5$) and binuclear osmium carbonyls $\text{Os}_2(\text{CO})_n$ ($n = 8, 9$) relating to systems for which experimental information is available. Among these osmium carbonyls, only $\text{Os}_2(\text{CO})_9$ appears to have been previously studied by other research groups using modern DFT methods.¹⁷

2. Theoretical Methods

DFT methods have been acknowledged to be a practical and effective tool for the computation of organometallic compounds.¹⁸⁻²⁴ Two DFT methods, namely, BP86 and MPW1PW91, were used in this study. The BP86 method is a pure DFT method that combines Becke's 1988 exchange functional with Perdew's 1986 correlation functional.^{25,26} The BP86 method has been shown to be reliable for first-row transition-metal organometallic systems.^{27,28} The MPW1PW91 method,²⁹ based on the generalized

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Table 2. IR-Active $\nu(\text{CO})$ Vibrational Frequencies (cm^{-1}) Predicted for $\text{Os}(\text{CO})_5$ (IR Intensities in Parentheses Are in km/mol)

	MPW1PW91	BP86	expt ²	expt ⁴²	expt ⁸	expt ¹³
5S-1 (D_{3h})	2099 (1473), 2143 (1621)	1980 (1243), 2018 (1387)	1991 (vs), 2034 (vs)	1993, 2035	1993 (vs), 2036 (vs)	1985.6, 1995.3, 2046.2
5S-2 (C_{4v})	2113 (1702), 2126 (1104), 2218 (1)	1992 (1430), 2001 (955), 2091 (5)				

gradient approximation, is a so-called second-generation³⁰ functional, which combines the modified Perdew–Wang exchange functional with Perdew–Wang’s 91 gradient-correlation functional.³¹ The MPW1PW91 method has been found to be more suitable for geometry optimization of the second- and third-row transition-metal systems,^{32,33} 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 Stuttgart–Dresden ECP plus DZ (SDD)³⁴ ECP basis set was used for the Os atoms. For the C and O atoms, double- ζ plus polarization (DZP) basis sets were used. They are Huzinaga–Dunning’s contracted double- ζ contraction sets^{35,36} plus a set of spherical harmonic d polarization functions with orbital exponents $\alpha_d(\text{C}) = 0.75$ and $\alpha_d(\text{O}) = 0.85$ 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 IR intensities were also evaluated analytically. All computations were carried out with the *Gaussian 03* program.³⁷ The fine (75, 302) grid is the default for evaluating integrals numerically. The finer (120, 974) grid³⁸ was used only for re-examination of the small imaginary vibrational frequencies. All of the predicted triplet structures are found to have negligible spin contamination, i.e., $S(S+1)$ is very close to the ideal value of 2.

3. Results

3.1. $\text{Os}(\text{CO})_5$. The global minimum **5S-1** (Figure 2 and Tables 1 and 2) found for $\text{Os}(\text{CO})_5$ is a D_{3h} trigonal bipyramid with all real vibrational frequencies. The Os–C (axial) distances of 1.966 Å (MPW1PW91) or 1.975 Å (BP86) and Os–C (equatorial) distances of 1.953 Å (MPW1PW91) or 1.962 Å (BP86) predicted for **5S-1** are very close to the 1.99 and 1.94 Å values found experimentally by gas-phase electron diffraction studies of $\text{Os}(\text{CO})_5$ vapor.³⁹

A second structure for $\text{Os}(\text{CO})_5$ is the C_{4v} square pyramid **5S-2** (Figure 2 and Tables 1 and 2), which is found to lie above **5S-1** by only 1.5 kcal/mol (Figure 2 and Table 1) with

a very small imaginary vibrational frequency at 33i (BP86; Table 1). This imaginary frequency appears to be significant because repeating the calculation with a finer grid (120, 974) increases the absolute value of this imaginary frequency to 35i cm^{-1} . Furthermore, the MP2 method also predicts an imaginary frequency of 38i cm^{-1} . Following the normal mode corresponding to this imaginary frequency leads to structure **5S-1** through a C_{2v} intermediate, suggesting a zero barrier Berry pseudorotation. The closeness in relative energies of the D_{3h} trigonal bipyramid **5S-1** and the C_{4v} square pyramid **5S-2** for $\text{Os}(\text{CO})_5$ is typical for five-coordinate complexes and relates to the stereochemical nonrigidity (fluxionality) for such structures.^{40,41}

For $\text{Os}(\text{CO})_5$, the IR-active $\nu(\text{CO})$ vibrational frequencies (cm^{-1}) predicted by the BP86 method are close to the experimental values (Table 2). However, the $\nu(\text{CO})$ frequencies predicted by the MPW1PW91 method are $\sim 100 \text{ cm}^{-1}$ higher than the experimental values (Table 2).^{2,8,13,42}

3.2. $\text{Os}(\text{CO})_4$. Four structures (two singlets and two triplets) are found for $\text{Os}(\text{CO})_4$ (Figure 3 and Tables 3 and 4). Three of these structures are predicted to be genuine minima with no imaginary vibrational frequencies. The D_{2d} singlet structure **4S-1** (Figure 3 and Table 3) is found to be the global minimum in accordance with the calculations and experiments of Zhou and Andrews.¹⁴ A D_{4h} square-planar structure **4S-2** is predicted to lie above **4S-1** by 7.2 kcal/mol (BP86 with two imaginary frequencies at 98i and 70i cm^{-1}). Following the corresponding normal mode leads to a C_{4v} structure and finally to **4S-1**. Also the singlet D_{2d} global minimum **4S-1** for $\text{Os}(\text{CO})_4$ is of higher symmetry than the singlet C_{2v} structure found by Ihee et al.^{43,44} in transient $\text{Fe}(\text{CO})_4$ from the photolysis of $\text{Fe}(\text{CO})_5$ using ultrafast electron diffraction.

The lowest-energy triplet structure for $\text{Os}(\text{CO})_4$, namely, the C_{2v} structure **4T-1** in the 3B_2 electronic state (Figure 3 and Table 3), has no imaginary vibrational frequencies and lies 12.9 kcal/mol (MPW1PW91) or 17.0 kcal/mol (BP86) above the global minimum **4S-1**. This structure can be derived from trigonal-bipyramidal $\text{Os}(\text{CO})_5$ (**5S-1**) by removal of one equatorial carbonyl group with concurrent partial movement of the axial carbonyl groups into the resulting void, so that the $C_{ax}\text{--Os--}C_{ax}$ angle bends from 180° to 155.4° (MPW1PW91) or 153.3° (BP86). A related C_{2v} structure was suggested for triplet $\text{Fe}(\text{CO})_4$ from a detailed study of its IR $\nu(\text{CO})$ frequencies in solid matrices and using time-resolved IR spectroscopy in the gas phase.⁴⁵

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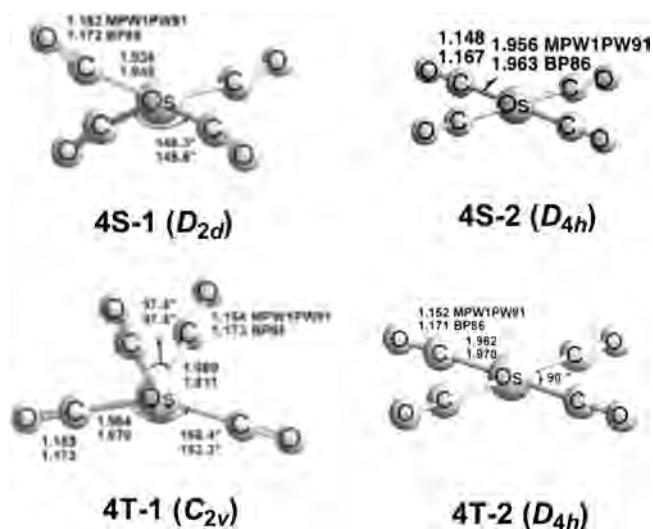


Figure 3. Four structures for Os(CO)₄.

A second triplet structure **4T-2** for Os(CO)₄ lies 21.0 kcal/mol (MPW1PW91) or 28.5 kcal/mol (BP86) above the global minimum **4S-1**. Structure **4T-2** is a D_{4h} square-planar structure in the $^3A_{2u}$ electronic state with no imaginary vibrational frequencies.

Zhou and Andrews¹⁴ report Os(CO)₄ as one of the products from the reaction of laser-ablated Os atoms with carbon monoxide in neon matrices at low temperature. They assign a strong $\nu(\text{CO})$ frequency at 1983 cm^{-1} to a D_{2d} isomer of Os(CO)₄ on the basis of their calculations of the strongest $\nu(\text{CO})$ frequency of D_{2d} Os(CO)₄ at 1975 cm^{-1} (Table 4). Their calculations of the $\nu(\text{CO})$ frequencies of singlet D_{2d} Os(CO)₄ similar to our **4S-1** isomer are in good agreement with our results (Table 4) using the same BP86 functional. Zhou and Andrews¹⁴ do not report triplet isomers of Os(CO)₄ analogous to our **4T-1** and **4T-2** isomers. However, the relatively high energies predicted here for **4T-1** and **4T-2** make them of questionable chemical relevance.

3.3. Os(CO)₃. Three structures (two singlets and one triplet) are found for Os(CO)₃ (Figure 4 and Tables 5 and 6). The global minimum of Os(CO)₃, namely, **3S-1** (Figure 4 and Table 5), has a C_s nonplanar T-shaped structure, which can be derived from the **5S-1** trigonal-bipyramidal structure of Os(CO)₅ (Figure 2) by removal of two equatorial carbonyl groups. The Os–C_{ax} bonds are then bent so that the C_{ax}–Os–C_{ax} angle is reduced from 180° in the trigonal bipyramid to 146.0° (MPW1PW91) or 144.4° (BP86). A related distorted T-shaped structure for Os(CO)₃ was also found by Zhou and Andrews.¹⁴

The next low-lying singlet structure **3S-2** of Os(CO)₃ (Figure 4 and Table 5) is an undistorted C_{2v} T-shaped structure, lying ~ 2.8 kcal/mol higher in energy above **3S-1**. Structure **3S-2** is predicted to be a transition state with one imaginary vibrational frequency, namely, 63i cm^{-1} (MPW1PW91) or 79i cm^{-1} (BP86). This is a true imaginary frequency because the finer grid computation did not change the value and the MP2 method predicts it to be 69i cm^{-1} . Following the corresponding normal mode leads to **3S-1**.

A C_{3v} pyramidal triplet structure **3T-1** in the 3A_2 electronic state was also found for Os(CO)₃. This structure is a true minimum with no imaginary vibrational frequencies and is found to lie in energy above the global minimum **3S-1** by 8.8 kcal/mol (MPW1PW91) or 11.2 kcal/mol (BP86).

Zhou and Andrews¹⁴ also report Os(CO)₃ as one of the products from the reaction of laser-ablated Os atoms with carbon monoxide in neon matrices at low temperatures. They assign strong $\nu(\text{CO})$ frequencies at 1966 and 1974 cm^{-1} to a planar T-shaped structure of Os(CO)₃ similar to **3S-2** on the basis of their calculations of the strongest $\nu(\text{CO})$ frequencies of C_{2v} Os(CO)₃ at 1973 and 1977 cm^{-1} (Table 6). Their calculations of the $\nu(\text{CO})$ frequencies of the singlet structures of Os(CO)₃ are in good agreement with our results (Table 6) using the same BP86 functional and the Los Alamos ECP plus DZ basis set for osmium. Zhou and Andrews¹⁴ do not report a triplet structure of Os(CO)₃ analogous to our **3T-1** structure.

3.4. Os₂(CO)₉. Five structures for Os₂(CO)₉ are discussed in this paper (Figure 5 and Tables 7 and 8). The lowest-energy Os₂(CO)₉ structure **9S-1** (Figure 5 and Table 7) with one bridging CO group and C_2 symmetry is the global minimum. A closely related more symmetrical C_{2v} structure **9S-2** is found within 0.2 kcal/mol of the global minimum **9S-1**. However, structure **9S-2** has a very small imaginary vibrational frequency at 12i cm^{-1} (BP86; Table 7). This frequency does not disappear when a finer integration grid (120, 974) is used. The corresponding normal mode of **9S-2** is related to inner rotation around the Os–Os bond and leads to the global minimum **9S-1** structure.

The predicted Os–Os bond lengths of 2.913 and 2.919 Å (MPW1PW91) or 2.961 and 2.969 Å (BP86) for **9S-1** and **9S-2** correspond to normal single bonds,^{46,47} thereby giving each of the two Os atoms the favored 18-electron configuration. The BP86 $\nu(\text{CO})$ frequencies for **9S-1** and **9S-2** (Table 8) are close to the reported^{7,8} experimental $\nu(\text{CO})$ frequencies (Table 8). Thus, the six experimental $\nu(\text{CO})$ frequencies of 1778 (m), 2000 (w), 2013 (s), 2024 (m), 2038 (vs), and 2080 (s) cm^{-1} can correspond to the calculated $\nu(\text{CO})$ frequencies for **9S-1** of 1808, {1986, 1988} unresolved, {1997, 2001} unresolved, 2012, 2017, and 2050 cm^{-1} with roughly the correct relative intensity pattern and an average error of ± 20 cm^{-1} . The $\nu(\text{CO})$ frequencies predicted by the MPW1PW91 method are found to be ~ 100 cm^{-1} higher than the experimental values.

Structure **9S-3** (C_s ; Figure 5 and Table 7) with two semibridging CO groups is predicted to lie in energy above the global minimum **9S-1** by 6.7 kcal/mol (MPW1PW91) or 4.7 kcal/mol (BP86). It is found to be a transition state with an imaginary vibrational frequency at 90i cm^{-1} (BP86). Following the corresponding normal mode collapses **9S-3** (C_s) first to a C_1 structure and finally to the C_2 global minimum **9S-1**. The predicted Os–Os bond distance of 2.892 Å (MPW1PW91) or 2.933 Å (BP86) in **9S-3** is consistent with the single bond required to give both Os atoms the favored 18-electron configuration. The predicted $\nu(\text{CO})$

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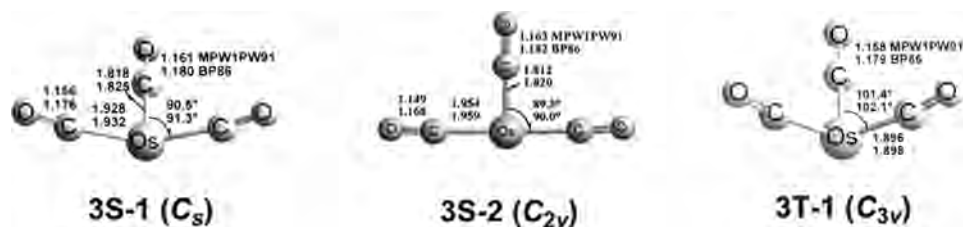
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Table 3. Total Energies (E , in hartree) and Relative Energies (ΔE , in kcal/mol) of $\text{Os}(\text{CO})_4^a$

		4S-1 (D_{2d})	4S-2 (D_{4h})	4T-1 (C_{2v})	4T-2 (D_{4h})
MPW1PW91	E	-544.11479	-544.10715	-544.09427	-544.08129
	ΔE	0	4.8	12.9	21.0
	Nimag	0	2 (79i, 57i)	0	0
	$\langle S^2 \rangle$	0	0	2.01	2.01
BP86	E	-544.37246	-544.36101	-544.34530	-544.32700
	ΔE	0	7.2	17.0	28.5
	Nimag	0	2 (98i, 70i)	0	0
	$\langle S^2 \rangle$	0	0	2.00	2.00

^a The number of imaginary vibrational frequencies (Nimag) is also listed.

**Figure 4.** Three structures predicted for $\text{Os}(\text{CO})_3$.**Table 4.** IR-Active $\nu(\text{CO})$ Vibrational Frequencies (cm^{-1}) Predicted for $\text{Os}(\text{CO})_4$ (IR Intensities in Parentheses Are in km/mol)

	MPW1PW91	BP86	BP86 work of Zhou and Andrews ¹⁴
4S-1 (D_{2d})	2090 (1994), 2115 (586)	1967 (1536), 1987 (548)	1975 (1443), 1995 (518)
4S-2 (D_{4h})	2104 (2376)	1986 (1928)	
4T-1 (C_{2v})	2084 (1931), 2095 (1124), 2101 (755), 2172 (63)	1954 (1552), 1972 (945), 1974 (653), 2039 (55)	
4T-2 (D_{4h})	2098 (1952)	1977 (1605)	

Table 5. Total Energies (E , in hartree) and Relative Energies (ΔE , in kcal/mol) of $\text{Os}(\text{CO})_3^a$

		3S-1 (C_s)	3S-2 (C_{2v})	3T-1 (C_{3v})
MPW1PW91	E	-430.73469	-430.73102	-430.72072
	ΔE	0	2.3	8.8
	Nimag	0	1 (63i)	0
	$\langle S^2 \rangle$	0	0	2.01
BP86	E	-430.95514	-430.94988	-430.93737
	ΔE	0	3.3	11.2
	Nimag	0	1 (79i)	0
	$\langle S^2 \rangle$	0	0	2.00

^a The number of imaginary vibrational frequencies (Nimag) and the spin contaminations $\langle S^2 \rangle$ for each structure are also listed.

frequencies at 1872 and 1877 cm^{-1} by BP86 (Table 8) correspond to the two semibridging CO groups.

A C_{2v} unbridged unsymmetrical $\text{Os}_2(\text{CO})_9$ structure **9S-4** (Figure 5 and Table 7), consisting of one $\text{Os}(\text{CO})_4$ unit and one $\text{Os}(\text{CO})_5$ unit, is predicted to lie in energy above the global minimum **9S-1** by 7.0 kcal/mol (MPW1PW91) or 7.9 kcal/mol (BP86) with all real vibrational frequencies. The Os–Os bond length in **9S-4** is found to be the longest of the five predicted $\text{Os}_2(\text{CO})_9$ structures, namely, 2.940 Å (MPW1PW91) or 2.989 Å (BP86), suggesting a relatively long single bond. This can correspond to an osmium \rightarrow osmium dative bond from an osmium lone electron pair in the $\text{Os}(\text{CO})_5$ unit to the coordinately unsaturated $\text{Os}(\text{CO})_4$ unit to give a structure represented as $(\text{OC})_5\text{Os} \rightarrow \text{Os}(\text{CO})_4$, in which both Os atoms have the 18-electron configuration. Heterobimetallic osmium–tungsten complexes of the type $(\text{R}_3\text{P})_2(\text{OC})_3\text{Os} \rightarrow \text{W}(\text{CO})_5$ with an osmium \rightarrow tungsten dative bond related to the $\text{Os}_2(\text{CO})_9$ structure **9S-4** have been reported and characterized structurally.⁴⁸ In addition, similar

heterometallic osmium–chromium complexes of the type $(\text{OC})_{5-x}(\text{tBuNC})_x\text{Os} \rightarrow \text{Cr}(\text{CO})_5$ ($x = 1, 2$) have been prepared and structurally characterized by X-ray diffraction.⁴⁹

A D_{3h} triply bridged structure $(\text{CO})_3\text{Os}(\mu\text{-CO})_3\text{Os}(\text{CO})_3$ (**9S-5**; Figure 5 and Table 7) similar to the well-known structure^{9,10} of $\text{Fe}_2(\text{CO})_9$ has also been found for $\text{Os}_2(\text{CO})_9$. Structure **9S-5** is predicted to lie in energy above **9S-1** by 11.6 kcal/mol (MPW1PW91) or 7.8 kcal/mol (BP86) and to have a small degenerate e'' imaginary vibrational frequency at 50i cm^{-1} (BP86). Using the finer (120, 974) integration grid has little effect on this imaginary vibrational frequency. Following one of the corresponding normal modes of **9S-5** leads first to **9S-3** and finally to the global minimum **9S-1**. The predicted Os–Os bond in **9S-5** at 2.793 Å (MPW1PW91) or 2.839 Å (BP86) is a little shorter than the other Os–Os single bonds found in this work because of the three bridging carbonyl groups. The three bridging carbonyl groups in **9S-5** are predicted to exhibit an IR-active e' $\nu(\text{CO})$ frequency at 1835 cm^{-1} (BP86; Table 8).

3.5. $\text{Os}_2(\text{CO})_8$. Six singlet and five triplet structures were found for $\text{Os}_2(\text{CO})_8$ (Figures 6 and 7 and Tables 9–11). The global minimum of $\text{Os}_2(\text{CO})_8$ is predicted to be a C_s singlet structure **8S-1** consisting of an $\text{Os}(\text{CO})_4$ unit and an $\text{Os}(\text{CO})_3$ unit connected by a single bridging CO group as well as a metal–metal bond (Figure 6 and Table 9). Conceptually, structure **8S-1** can be generated from the C_{2v} structure **9S-2** of $\text{Os}_2(\text{CO})_9$ by removal of a single terminal CO group. The Os–Os distance of **8S-1** (C_s) is found to be 0.07 Å shorter than that for **9S-2** (C_{2v}), consistent with a normal single bond, thereby giving one Os atom an 18-electron configuration (the

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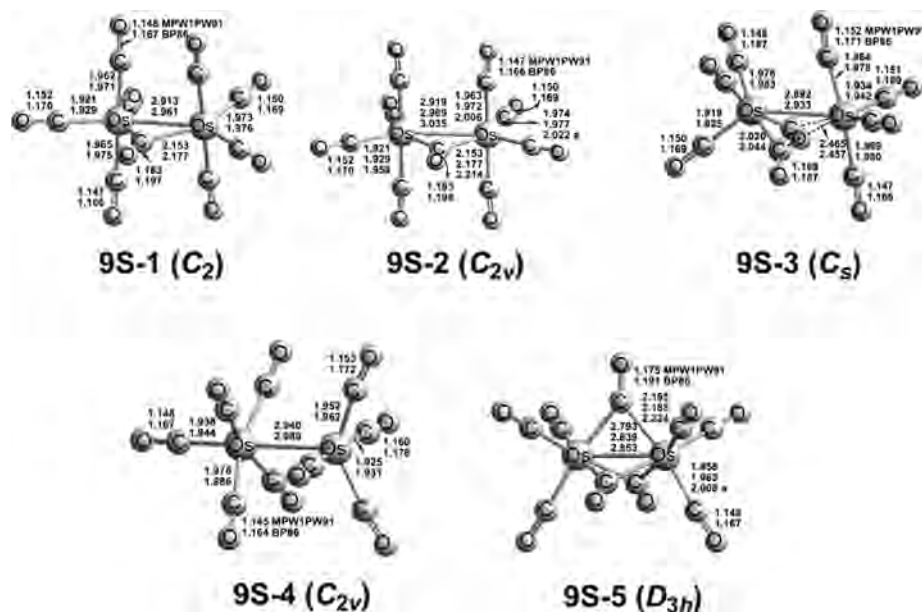


Figure 5. Five structures for $\text{Os}_2(\text{CO})_9$. In structures **9S-2** and **9S-5**, the third distance is taken from ref 17.

Table 6. Active IR $\nu(\text{CO})$ Vibrational Frequencies (cm^{-1}) Predicted for $\text{Os}(\text{CO})_3$ (IR Intensities in Parentheses Are in km/mol)

	MPW1PW91	BP86	BP86 calculations of Zhou and Andrews ¹⁴
3S-1 (C_s)	2066 (2114), 2074 (952), 2165 (187)	1942 (1606), 1961 (533), 2037 (171)	1949 (1512), 1969 (699), 2043 (171)
3S-2 (C_{2v})	2075 (962), 2094 (2411), 2204 (23)	1969 (756), 1970 (1938), 2074 (21)	1973 (1846), 1977 (744)
3T-1 (C_{3v})	2049 (1554), 2049 (1553), 2125 (303)	1925 (1226), 1925 (1227), 1991 (217)	

Table 7. Total Energies (E , in hartree) and Relative Energies (ΔE , in kcal/mol) of $\text{Os}_2(\text{CO})_9$ ^a

		9S-1 (C_2)	9S-2 (C_{2v})	9S-3 (C_s)	9S-4 (C_{2v})	9S-5 (D_{3h})
MPW1PW91	E	-1201.63639	-1201.63619	-1201.62577	-1201.62519	-1201.61788
	ΔE	0	0.1	6.7	7.0	11.6
	Nimag	0	1 (14i)	1 (116i)	0	2 (55i, 55i)
	Os–Os	2.913	2.919	2.892	2.940	2.793
BP86	E	-1202.17119	-1202.17093	-1202.16370	-1202.15866	-1202.15880
	ΔE	0	0.2	4.7	7.9	7.8
	Nimag	0	1 (12i)	1 (90i)	0	2 (50i, 50i)
	Os–Os	2.961	2.969	2.933	2.989	2.839

^a The number of imaginary vibrational frequencies (Nimag) and the Os–Os bond distance for each structure are also listed.

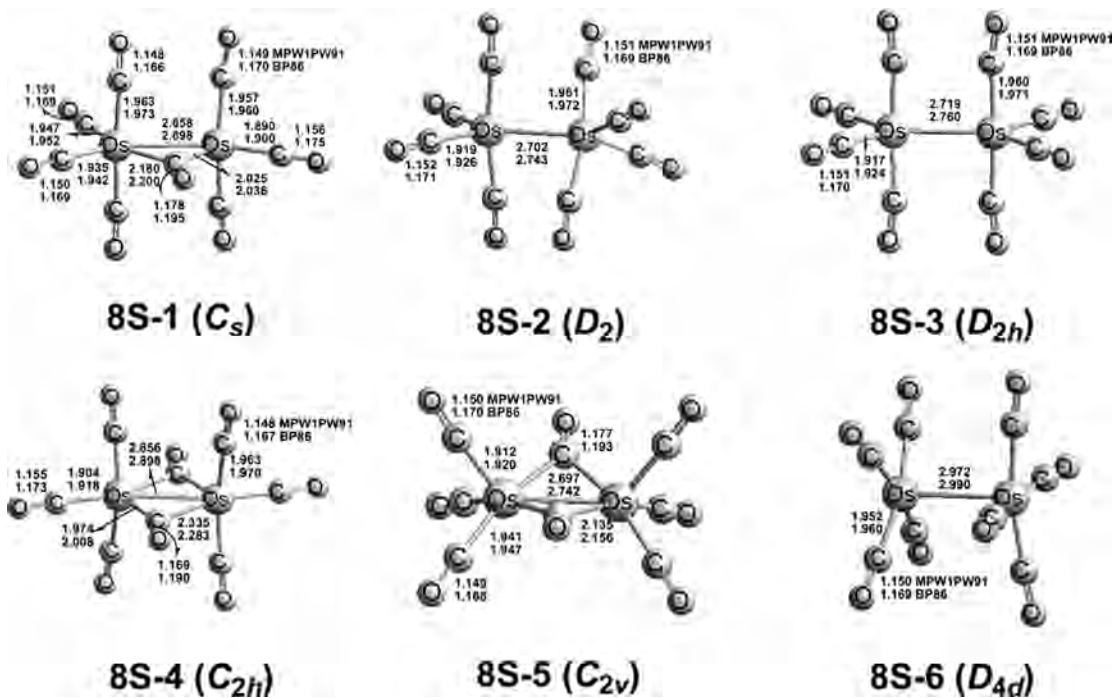
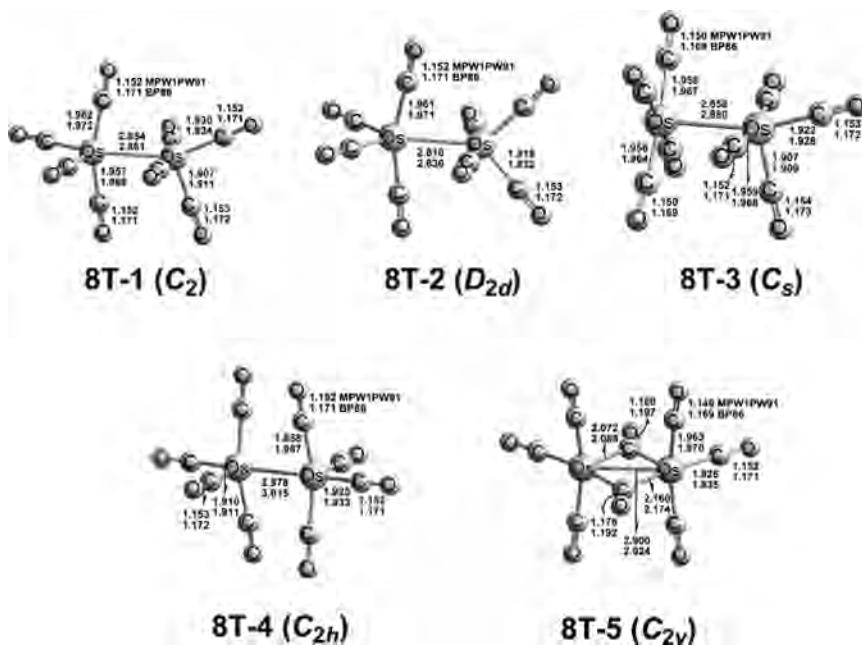
Table 8. IR-Active $\nu(\text{CO})$ Vibrational Frequencies (cm^{-1}) Predicted for $\text{Os}_2(\text{CO})_9$ (IR Intensities in Parentheses Are in km/mol ; Bridging $\nu(\text{CO})$ Frequencies Are in Boldface)

	MPW1PW91	BP86	Expt. ^{7,8}
9S-1 (C_2)	1896 (704) , 2107 (133), 2112 (43), 2120 (1786), 2126 (770), 2139 (188), 2145 (2556), 2178 (1207), 2230 (5)	1808 (570) , 1986 (77), 1988 (19), 1997 (1607), 2001 (682), 2012 (98), 2017 (2162), 2050 (1143), 2098 (4)	1778 (m) , 2000 (w), 2013 (s), 2024 (m), 2038 (vs), 2080 (s)
9S-2 (C_{2v})	1895 (706) , 2106 (115), 2119 (1736), 2125 (765), 2140 (252), 2146 (2595), 2179 (1175), 2231 (5)	1806 (575) , 1985 (41), 1997 (1563), 2000 (677), 2013 (140), 2019 (2197), 2052 (1121), 2099 (3)	
9S-3 (C_s)	1984 (791) , 1988 (414) , 2106 (335), 2117 (1006), 2129 (321), 2132 (1998), 2135 (891), 2168 (1962), 2217 (9)	1872 (701) , 1877 (300) , 1980 (294), 1998 (660), 2006 (764), 2006 (907), 2007 (1153), 2040 (1854), 2084 (6)	
9S-4 (C_{2v})	2054 (1095), 2078 (388), 2079 (903), 2146 (746), 2150 (1508), 2152 (1743), 2156 (854), 2241 (69)	1943 (832), 1961 (687), 1963 (428), 2018 (808), 2023 (1309), 2024 (1525), 2032 (699), 2109 (74)	
9S-5 (D_{3h})	1925 (1073) , 2142 (1733), 2171 (2342)	1835 (824) , 2013 (1492), 2040 (2154)	

“left” Os atom in Figure 6) and the other Os atom a 16-electron configuration (the “right” Os atom in Figure 6).

The next higher predicted structure for $\text{Os}_2(\text{CO})_8$ (Figure 6 and Table 9) is a D_2 singlet structure **8S-2** with only terminal carbonyl groups and all real vibrational frequencies.

The energy of **8S-2** is within ~ 1 kcal/mol of the global minimum **8S-1**. A higher-symmetry (D_{2h}) unbridged singlet isomer **8S-3** closely related to **8S-2** is also found for $\text{Os}_2(\text{CO})_8$ with an energy only ~ 1.2 kcal/mol above **8S-2**. Structure **8S-3** is found to have a very small imaginary

Figure 6. Six singlet structures of $\text{Os}_2(\text{CO})_8$.Figure 7. Five triplet structures of $\text{Os}_2(\text{CO})_8$.

vibrational frequency at $19i \text{ cm}^{-1}$ (BP86) corresponding to internal rotation around the Os–Os bond. By following the corresponding normal mode, **8S-3** collapses to **8S-2**. The Os–Os bond lengths for **8S-2** and **8S-3** are predicted at 2.702 and 2.719 \AA (MPW1PW91) or 2.743 and 2.760 \AA (BP86), corresponding to the Os=Os double bond required to give each of the two Os atoms the favored 18-electron configuration. The theoretical $\nu(\text{CO})$ frequencies for **8S-2** and **8S-3** with the BP86 method are found close to the experimentally^{11–13} reported $\nu(\text{CO})$ frequencies (Table 10). Thus, the three experimental $\nu(\text{CO})$ frequencies at 2005 ± 2 , 2021 ± 3 , and $2058 \pm 2 \text{ cm}^{-1}$ may correspond to the calculated $\nu(\text{CO})$ frequencies of 1989, 1999, and 2031 cm^{-1}

for **8S-2** with an average error of $\pm 22 \text{ cm}^{-1}$. The IR $\nu(\text{CO})$ vibrational frequencies (cm^{-1}) predicted by the MPW1PW91 method (provided in the Supporting Information) are found to be roughly 100 cm^{-1} higher than those by the BP86 method.

A doubly CO-bridged singlet structure **8S-4** (C_{2h} ; Figure 6 and Table 9) is also found to be a genuine minimum for $\text{Os}_2(\text{CO})_8$, lying in energy 4.8 kcal/mol (MPW1PW91) or 0.8 kcal/mol (BP86) above the global minimum **8S-1**. In **8S-4**, the central Os(μ -CO)₂Os unit is coplanar. The Os–Os bond distance in **8S-4** is predicted to be 2.856 \AA (MPW1PW91) or 2.898 \AA (BP86).

Table 9. Total Energies (E , in hartree) and Relative Energies (ΔE , in kcal/mol) of the Singlet Structures of $\text{Os}_2(\text{CO})_8^a$

	8S-1 (C_s)	8S-2 (D_2)	8S-3 (D_{2h})	8S-4 (C_{2h})	8S-5 (C_{2v})	8S-6 (D_{4d})
MPW1PW91						
E	-1088.28547	-1088.28380	-1088.28181	-1088.27780	-1088.26801	-1088.24873
ΔE	0	1.0	2.3	4.8	11.0	23.1
Nimag	0	0	1 (2 <i>i</i>)	0	1(45 <i>i</i>)	2 (14 <i>i</i> , 14 <i>i</i>)
Os–Os	2.858	2.702	2.719	2.856	2.697	2.972
BP86						
E	-1088.79101	-1088.78920	-1088.78740	-1088.78980	-1088.77799	-1088.76076
ΔE	0	1.1	2.3	0.8	8.2	19.0
Nimag	0	0	1 (19 <i>i</i>)	0	1(32 <i>i</i>)	2 (12 <i>i</i> , 12 <i>i</i>)
Os–Os	2.898	2.743	2.760	2.898	2.742	2.990

^a The number of imaginary vibrational frequencies (Nimag) and the Os–Os bond distance for each structure are also listed.

Table 10. IR-Active $\nu(\text{CO})$ Vibrational Frequencies (cm^{-1}) Predicted for $\text{Os}_2(\text{CO})_8$ by the BP86 Method (IR Intensities in Parentheses Are in km/mol , Bridging $\nu(\text{CO})$ Frequencies Are in Boldface, and Experimental Results Are in Italics)

	BP86
8S-1 (C_s)	1825 (527) , 1964 (410), 1977 (548), 1997 (1011), 2011 (1849), 2013 (120), 2034 (1327), 2089 (95)
8S-2 (D_2)	1968 (11), 1980 (55), 1987 (109) 1989 (1907), 1999 (2146), 2031 (1925)
8S-3 (D_{2h}) expt ^{11–13}	1984 (49), 1991 (1921), 2001 (2180), 2037 (1969) 2007, 2023, 2060; ¹¹ 2003, 2018, 2058; ¹² 2007.1, 2023.4, 2056.8 ¹³
8S-4 (C_{2h})	1866 (1004) , 1987 (1299), 2004 (2386), 2033 (1861)
8S-5 (C_{2v})	1808 (871) , 1844 (156) , 1991 (13), 2001 (1703), 2009 (1505), 2039 (1884), 2072 (18)
8S-6 (D_{4d})	1990 (2655), 1990 (2655), 2034 (2198)
8T-1 (C_2)	1965 (71), 1965 (91), 1981 (1525), 1985 (1647), 1989 (272), 1994 (1172), 2024 (1096), 2065 (5)
8T-2 (D_{2d})	1966 (78), 1966 (78), 1985 (1990), 1985 (1990), 1989 (734), 2021 (1146)
8T-3 (C_s)	1957 (63), 1970 (94), 1981 (648), 1989 (1640), 1992 (2304), 2029 (1038), 2087 (50)
8T-4 (C_{2h})	1971 (563), 1985 (2253), 1986 (1312), 2028 (1569)
8T-5 (C_{2v})	1818 (670) , 1833 (121) , 1985 (340), 1993 (2455), 1994 (494), 2028 (1783), 2074 (3)

Another doubly CO-bridged structure (**8S-5** in Figure 6 and Table 9) of C_{2v} symmetry was also found for $\text{Os}_2(\text{CO})_8$ at 11.0 kcal/mol (MPW1PW91) or 8.2 kcal/mol (BP86) in energy above the global minimum **8S-1** of $\text{Os}_2(\text{CO})_8$. Structure **8S-5** is found to have a very small imaginary vibrational frequency at $32i \text{ cm}^{-1}$ (BP86), which decreases slightly to $29i \text{ cm}^{-1}$ when the finer integration grid (120, 974) is used. Following the corresponding normal mode leads to structure **8S-2** (D_2), with the bridging carbonyl groups in **8S-5** becoming terminal carbonyl groups. In **8S-5**, the central $\text{Os}(\mu\text{-CO})_2\text{Os}$ unit is not planar. The Os–Os bond distance in **8S-5** is found at 2.697 Å (MPW1PW91) or 2.742 Å (BP86), suggesting the Os=Os double bond required to give both Os atoms the favored 18-electron configurations.

The final predicted singlet structure **8S-6** of $\text{Os}_2(\text{CO})_8$ (Figure 6 and Table 9) is a higher-symmetry unbridged D_{4d} structure of significantly higher energy at 23.1 kcal/mol (MPW1PW91) or 19.0 kcal/mol (BP86) above the **8S-1** $\text{Os}_2(\text{CO})_8$ global minimum (Figure 6 and Table 9). Structure **8S-6** has a very small degenerate e_2 imaginary vibrational frequency at $12i \text{ cm}^{-1}$ (BP86), which increases to $24i \text{ cm}^{-1}$ (BP86) when a finer (120, 974) integration grid is used. Following the corresponding normal mode reduces the symmetry from D_{4d} to D_2 to give the lowest-energy unbridged $\text{Os}_2(\text{CO})_8$ structure **8S-2**.

Five triplet structures for $\text{Os}_2(\text{CO})_8$ were found (Figure 7 and Tables 10 and 11). The Os–Os distances in all of the triplet structures fall in the range 2.81–3.01 Å, consistent with the single bonds required to give both Os atoms 17-electron configurations, leading to two unpaired electrons and thus triplet spin multiplicity.

The lowest-lying triplet structure **8T-1** of $\text{Os}_2(\text{CO})_8$ (Figure 7 and Table 11) is predicted to be an unbridged C_2 structure in the 3B electronic state with all real vibrational frequencies. It is predicted to lie 8.4 kcal/mol (MPW1PW91) or 12.3 kcal/mol (BP86) in energy above the global minimum **8S-1** of $\text{Os}_2(\text{CO})_8$.

The second-lowest-lying triplet structure **8T-2** (Figure 7 and Table 11) with D_{2d} symmetry in the 3A_2 electronic state differs only slightly from **8T-1**. It is predicted to lie 9.4 kcal/mol (MPW1PW91) or 12.6 kcal/mol (BP86) above the global minimum **8S-1** and has a small degenerate imaginary vibrational frequency at $20i \text{ cm}^{-1}$ (BP86; Table 11). Using a finer grid (120, 974) decreases this imaginary vibrational frequency decreases only slightly to $17i \text{ cm}^{-1}$ (BP86). By following the corresponding normal mode, structure **8T-2** collapses to **8T-1**.

The next two triplet structures of $\text{Os}_2(\text{CO})_8$, namely, **8T-3** (C_s , $^3A'$ state) and **8T-4** (C_{2h} , 3B_u state) (Figure 7 and Table 11), are another pair of unbridged triplet isomers consisting of two $\text{Os}(\text{CO})_4$ units connected by an Os–Os single bond. Structure **8T-3** (C_s) is found to be a genuine minimum, lying in energy above the global minimum **8S-1** by 12.1 kcal/mol (MPW1PW91) or 15.6 kcal/mol (BP86). Structure **8T-4** (C_{2h}) is predicted to lie still higher in energy at 16.1 kcal/mol (MPW1PW91) or 19.9 kcal/mol (BP86) above the global minimum **8S-1**. The small imaginary vibrational frequency of $21i \text{ cm}^{-1}$ in **8T-4** (BP86; Table 11) decreases to $20i \text{ cm}^{-1}$ (BP86) when the finer integration grid (120, 974) is used. Following the corresponding normal mode leads to the lowest-energy triplet structure **8T-1** with reduction of the symmetry from C_{2h} to C_2 .

Structure **8T-5** (C_{2v} , 3B_2 state; Figure 7 and Table 11) is the only triplet structure found with bridging carbonyl groups. It is predicted to be a genuine minimum but at a relatively high energy of 22.9 kcal/mol (MPW1PW91) or 21.6 kcal/mol (BP86) above the $\text{Os}_2(\text{CO})_8$ global minimum **8S-1**.

3.6. Dissociation Energies. Table 12 summarizes some dissociation energies involving the binuclear osmium carbonyl derivatives $\text{Os}_2(\text{CO})_n$ ($n = 8, 9$). The dissociation of

Table 11. Total Energies (E , in hartree) and Relative Energies (ΔE , in kcal/mol) of the Triplet Structures of $\text{Os}_2(\text{CO})_8^d$

		8T-1 (C_2)	8T-2 (D_{2d})	8T-3 (C_3)	8T-4 (C_{2h})	8T-5 (C_{2v})
MPW1PW91	E	-1088.27215	-1088.27048	-1088.26623	-1088.25980	-1088.24893
	ΔE	8.4	9.4	12.1	16.1	22.9
	Nimag	0	2 (28i, 28i)	0	1 (25i)	0
	Os–Os	2.854	2.810	2.858	2.978	2.900
	$\langle S^2 \rangle$	2.01	2.01	2.01	2.01	2.02
BP86	E	-1088.77137	-1088.77088	-1088.76620	-1088.75925	-1088.75664
	ΔE	12.3	12.6	15.6	19.9	21.6
	Nimag	0	2 (20i, 20i)	0	1 (21i)	0
	Os–Os	2.861	2.830	2.880	3.015	2.924
	$\langle S^2 \rangle$	2.00	2.00	2.00	2.00	2.00

^a The number of imaginary vibrational frequencies (Nimag) and the Os–Os bond distance for each structure are also listed.

Table 12. Dissociation Energies (kcal/mol) for $\text{Os}(\text{CO})_n$ and $\text{Os}_2(\text{CO})_n$

	MPW1PW91	BP86
$\text{Os}_2(\text{CO})_9$ (9S-1) \rightarrow $\text{Os}_2(\text{CO})_8$ (8S-1) + CO	32.5	30.1
$\text{Os}_2(\text{CO})_9$ (9S-1) \rightarrow $\text{Os}(\text{CO})_5$ (5S-1) + $\text{Os}(\text{CO})_4$ (4S-1)	27.7	21.7
$\text{Os}_2(\text{CO})_9$ (9S-4) \rightarrow $\text{Os}(\text{CO})_5$ (5S-1) + $\text{Os}(\text{CO})_4$ (4S-1)	20.6	13.9
$\text{Os}_2(\text{CO})_8$ (8S-1) \rightarrow $\text{Os}(\text{CO})_5$ (5S-1) + $\text{Os}(\text{CO})_3$ (3S-1)	46.0	45.0
$\text{Os}_2(\text{CO})_8$ (8S-1) \rightarrow $2\text{Os}(\text{CO})_4$ (4S-1)	35.1	28.9
$\text{Os}_2(\text{CO})_8$ (8S-2) \rightarrow $2\text{Os}(\text{CO})_4$ (4S-1)	34.0	27.8
$\text{Os}(\text{CO})_5$ (5S-1) \rightarrow $\text{Os}(\text{CO})_4$ (4S-1) + CO	39.9	37.3
$\text{Os}(\text{CO})_4$ (4S-1) \rightarrow $\text{Os}(\text{CO})_3$ (3S-1) + CO	50.7	53.4
$\text{Os}(\text{CO})_3$ (3S-1) \rightarrow $\text{Os}(\text{CO})_2$ + 3CO	154.7	180.7

the global minimum **9S-1** of $\text{Os}_2(\text{CO})_9$ into the mononuclear fragments $\text{Os}(\text{CO})_5 + \text{Os}(\text{CO})_4$ is seen to be a less energetically demanding process than the dissociation of one carbonyl group from $\text{Os}_2(\text{CO})_9$ (**9S-1**) to give $\text{Os}_2(\text{CO})_8$ (**8S-1**). Even the dissociation of the higher-energy unbridged isomer **9S-4** of $\text{Os}_2(\text{CO})_9$ into its components $\text{Os}(\text{CO})_5 + \text{Os}(\text{CO})_4$ is an endothermic process by 20.6 kcal/mol (MPW1PW91) or 13.9 kcal/mol (BP86). This necessarily implies that the reverse reaction, namely, the complexation of the coordinatively unsaturated $\text{Os}(\text{CO})_4$ (**4S-1**) with an $\text{Os}(\text{CO})_5$ “ligand” (**5S-1**), is an exothermic process. This thermodynamic analysis demonstrates the basicity of a “lone” electron pair on the coordinatively saturated $\text{Os}(\text{CO})_5$.

There are two obvious alternative pathways for the dissociation of the binuclear $\text{Os}_2(\text{CO})_8$ into mononuclear fragments, namely, the symmetrical dissociation into $2\text{Os}(\text{CO})_4$ or the unsymmetrical dissociation into $\text{Os}(\text{CO})_5 + \text{Os}(\text{CO})_3$. The results summarized in Table 12 indicate that the symmetrical dissociation of the global minimum **8S-1** of $\text{Os}_2(\text{CO})_8$ is easier than the unsymmetrical dissociation by 10.9 kcal/mol (MPW1PW91) or 16.1 kcal/mol (BP86).

The CO dissociation energies for the global minima of the mononuclear osmium carbonyls $\text{Os}(\text{CO})_n$ ($n = 3-5$) have also been examined (Table 12). The CO dissociation energy of 38 ± 2 kcal/mol for $\text{Os}(\text{CO})_5$ is only slightly lower than the reported⁵⁰ CO dissociation energy of 41 ± 2 kcal/mol for $\text{Fe}(\text{CO})_5$. Furthermore, the dissociation energy for the loss of the second carbonyl group from $\text{Os}(\text{CO})_5$, as indicated by the 52 ± 2 kcal/mol CO dissociation energy of the $\text{Os}(\text{CO})_4$ isomer **4S-1**, is significantly higher than that for

the loss of its first CO group in accordance with stronger Os \rightarrow CO π back-bonding in $\text{Os}(\text{CO})_4$ relative to $\text{Os}(\text{CO})_5$. This is also consistent with the lower $\nu(\text{CO})$ frequencies of $\text{Os}(\text{CO})_4$ (Table 4) relative to $\text{Os}(\text{CO})_5$ (Table 2).

4. Discussion

4.1. Mononuclear Derivatives. The lowest-energy structure for $\text{Os}(\text{CO})_5$ is the expected D_{3h} trigonal bipyramid **5S-1** (Figure 2) in accordance with experimental results.^{2,39} However, the C_{4v} square-pyramidal structure **5S-2** of $\text{Os}(\text{CO})_5$ is very close in energy to the trigonal bipyramid **5S-1**, suggesting a highly fluxional system as is typical for five-coordinate complexes.^{40,41}

The lowest-energy structure **4S-1** (Figure 3) for the coordinatively unsaturated $\text{Os}(\text{CO})_4$ can be derived from an idealized tetrahedral structure by a Jahn–Teller distortion, reducing the symmetry from T_d to D_{2d} . The higher-energy triplet C_{2v} structure **4T-1** for $\text{Os}(\text{CO})_4$ can be derived from the D_{3h} trigonal-bipyramidal structure **5S-1** for $\text{Os}(\text{CO})_5$ by loss of an equatorial carbonyl group. The highest energy of the structures found for $\text{Os}(\text{CO})_4$, namely, **4T-2** (Figure 3), has the D_{4h} square-planar configuration expected for a four-coordinate complex of a d^8 metal such as $\text{Os}(0)$. However, **4T-2** has triplet spin multiplicity in contrast to the singlet spin multiplicity of the large number of known square-planar complexes of other d^8 metals, such as $\text{Ir}(\text{I})$, $\text{Pt}(\text{II})$, and $\text{Au}(\text{III})$ in the same row of the Periodic Table as $\text{Os}(0)$. A singlet D_{4h} structure **4S-2** was also found for $\text{Os}(\text{CO})_4$ but only as a transition state rather than a true minimum.

The loss of two equatorial carbonyl groups from the D_{3h} trigonal-bipyramidal structure **5S-1** for $\text{Os}(\text{CO})_5$ leads to the T-shaped C_{2v} structure **3S-2** (Figure 4) for $\text{Os}(\text{CO})_3$, maintaining the almost linear $\text{OC}_{\text{ax}}-\text{Os}-\text{C}_{\text{ax}}\text{O}$ configuration of the original $\text{Os}(\text{CO})_5$ structure **5S-1**. However, structure **3S-2** is unstable with respect to bending of the $\text{OC}_{\text{ax}}-\text{Os}-\text{C}_{\text{ax}}\text{O}$ unit to a $\text{C}_{\text{ax}}-\text{Os}-\text{C}_{\text{ax}}$ angle of 146.0° (MPW1PW91) or 144.4° (BP86) to give the structure **3S-1** (Figure 4), lying 2.3 kcal/mol (MPW1PW91) or 3.3 kcal/mol (BP86) below **3S-2**. The higher-energy triplet structure **3T-1** for $\text{Os}(\text{CO})_3$ (Figure 4) with 3-fold C_{3v} symmetry can be derived from a hypothetical T_d tetrahedral $\text{Os}(\text{CO})_4$ structure by loss of one of its carbonyl groups.

4.2. Binuclear Derivatives. The lowest-energy structure for $\text{Os}_2(\text{CO})_9$ is the singly bridged structure $\text{Os}_2(\text{CO})_8(\mu\text{-CO})$ (**9S-1** or **9S-2** in Figure 5) in accordance with experimental results.^{7,8} The triply bridged structure $\text{Os}_2(\text{CO})_6(\mu\text{-CO})_3$ (**9-5**

(50) Ehlers, A. W.; Frenking, G. *Organometallics* **1995**, *14*, 423.

in Figure 5) analogous to the well-established known structure for $\text{Fe}_2(\text{CO})_9$ is found to lie 11.6 kcal/mol (MPW1PW91) or 7.8 kcal/mol (BP86) above the singly bridged global minimum **9S-1**. Furthermore, the triply bridged structure **9S-5** for $\text{Os}_2(\text{CO})_9$ is a transition state rather than a true minimum because following its imaginary vibrational frequency leads ultimately to the global minimum **9S-1**. Our results on $\text{Os}_2(\text{CO})_9$ are in good agreement with the DFT studies of Reinhold et al.,¹⁷ who find the triply bridged $\text{Os}_2(\text{CO})_9$ structure similar to **9S-5** to lie 7.1 kcal/mol above the singly bridged structure **9S-1** using a functional closely related to BP86 in the Amsterdam density functional program package.

An unbridged structure **9S-4**, not considered in any previous work, is also found to be a true minimum for $\text{Os}_2(\text{CO})_9$ without any imaginary vibrational frequencies. This structure lies 7.0 kcal/mol (MPW1PW91) or 7.9 kcal/mol (BP86) above the global minimum **9S-1**. This structure may be derived from the C_{4v} square-pyramidal structure **5S-2** (Figure 2) of $\text{Os}(\text{CO})_5$ by replacement of its apical carbonyl group with an $\text{Os}(\text{CO})_5$ "ligand" using one of the lone pairs on its Os atom to give an $(\text{OC})_5\text{Os} \rightarrow \text{Os}(\text{CO})_4$ complex. Substitution products of $\text{Os}(\text{CO})_5$ of the type $L_n\text{Os}(\text{CO})_{5-n}$ are known to be similar ligands in structurally characterized binuclear heterometallic complexes of the types $(\text{R}_3\text{P})_2(\text{OC})_3\text{Os} \rightarrow \text{W}(\text{CO})_5$ ⁴⁸ and $(\text{OC})_{5-x}(\text{tBuNC})_x\text{Os} \rightarrow \text{Cr}(\text{CO})_5$ ($n = 1, 2$).⁴⁹

The lowest-energy structure **8S-1** for the unsaturated $\text{Os}_2(\text{CO})_8$ is a singly bridged structure $(\text{OC})_3\text{Os}(\mu-$

$\text{CO})\text{Os}(\text{CO})_4$ (**8S-1** in Figure 6), which can be derived from the global minimum structure $\text{Os}_2(\text{CO})_8(\mu-\text{CO})$ for $\text{Os}_2(\text{CO})_9$ (**9S-1** in Figure 5) by loss of one of its terminal carbonyl groups. This structure has not yet been observed experimentally. Instead, the $\text{Os}_2(\text{CO})_8$ structure found experimentally has no bridging carbonyl groups and appears to correspond to the unbridged **8S-2** on the basis of its IR $\nu(\text{CO})$ frequencies, which are in good agreement with the predicted $\nu(\text{CO})$ frequencies. The singly bridged **8S-2** for $\text{Os}_2(\text{CO})_8$ is predicted to lie only ~ 1 kcal/mol above the singly bridged global minimum **8S-1**.

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Supporting Information Available: Theoretical harmonic vibrational frequencies for $\text{Os}(\text{CO})_5$ (2 structures), $\text{Os}(\text{CO})_4$ (3 structures), $\text{Os}(\text{CO})_3$ (3 structures), $\text{Os}_2(\text{CO})_9$ (5 structures), and $\text{Os}_2(\text{CO})_8$ (13 structures) using the BP86 method (Tables S1–S7), theoretical Cartesian coordinates for $\text{Os}(\text{CO})_5$ (2 structures), $\text{Os}(\text{CO})_4$ (3 structures), $\text{Os}(\text{CO})_3$ (3 structures), $\text{Os}_2(\text{CO})_9$ (5 structures), and $\text{Os}_2(\text{CO})_8$ (13 structures) using the MPW1PW91 method (Tables S8–S33), and the complete *Gaussian 03* reference (ref 37). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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