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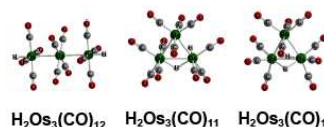
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Mei Xiang, Nan Li,* R. Bruce King,*
and Henry F. Schaefer III

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Metal Triangles versus Metal Chains and Terminal versus Bridging Hydrogen Atoms in Trinuclear Osmium Carbonyl Hydride Chemistry

Mei Xiang,^a Nan Li,^{*a} R. Bruce King,^{*b} and Henry F. Schaefer, III^b

^aState Key Laboratory of Explosion Science and Technology, School of Mechatronics Engineering, Beijing Institute of Technology, Beijing, 100081, P. R. China

^bDepartment of Chemistry and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602, USA

Abstract

The chemistry of trinuclear osmium carbonyl hydrides is a rich area with the three $\text{H}_2\text{Os}_3(\text{CO})_n$ derivatives ($n = 12, 11, 10$) all being known stable compounds ultimately obtained from $\text{Os}_3(\text{CO})_{12}$ and hydrogen under various conditions. Density functional theory studies on the $\text{H}_2\text{Os}_3(\text{CO})_n$ systems ($n = 12, 11, 10, 9, 8$) correctly predict the species previously reported experimentally for $n = 12, 11$, and 10. These include a linear structure for $\text{H}_2\text{Os}_3(\text{CO})_{12}$ and triangular structures for $\text{H}_2\text{Os}_3(\text{CO})_{11}$ and $\text{H}_2\text{Os}_3(\text{CO})_{10}$. However, the $\text{H}_2\text{Os}_3(\text{CO})_{11}$ system is predicted to be a fluxional system with the four low energy isomers lying within 2 kcal/mol of energy. Three of these $\text{H}_2\text{Os}_3(\text{CO})_{11}$ isomers, all with one terminal hydrogen and one bridging hydrogen, have been observed experimentally by NMR. In addition, the lowest energy isomer has been isolated and structurally characterized by X-ray crystallography. In contrast to $\text{H}_2\text{Os}_3(\text{CO})_{11}$, the lowest energy $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure, namely the known structure with an Os=Os edge bridged by both hydrogen atoms and all terminal CO groups, lies ~10 kcal/mol below the next lowest energy isomer. The predicted CO dissociation energies of the $\text{H}_2\text{Os}_3(\text{CO})_n$ derivatives ($n = 12, 11, 10$) suggest this $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure to be the “thermodynamic sink” in the $\text{H}_2\text{Os}_3(\text{CO})_n$ systems, consistent with its synthesis from $\text{Os}_3(\text{CO})_{12}$ and H_2 at 120°C and atmospheric pressure. The lowest energy structures of the more highly unsaturated $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 9, 8$) can be derived from this ($\mu\text{-H}$) $_2\text{Os}_3(\text{CO})_{10}$ structure by removal of CO groups from the osmium atom remote to the doubly bridged Os=Os edge of the Os_3 triangle, with relatively little change in the central ($\mu\text{-H}$) $_2\text{Os}_3$ triangle geometry.

1. Introduction

The metal carbonyl hydrides of the third row transition metals are so stable that they can sometimes even be synthesized by reactions of the metal carbonyls with gaseous hydrogen at atmospheric pressure and elevated temperatures. The first such compound to be synthesized in this manner was the colorless trinuclear rhenium carbonyl hydride $(\mu\text{-H})_3\text{Re}_3(\text{CO})_{12}$, obtained from $\text{Re}_2(\text{CO})_{10}$ and gaseous hydrogen.¹ Later the purple osmium carbonyl hydride $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ was analogously synthesized from $\text{Os}_3(\text{CO})_{12}$ and hydrogen at 120°C at atmospheric pressure in boiling octane.²

Subsequent research has shown the chemistry of trinuclear osmium carbonyl hydrides to be particularly extensive. Thus the three derivatives $\text{H}_2\text{Os}_3(\text{CO})_{12}$, $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{11}$, and $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ are all stable compounds with the loss of a CO group being accompanied by conversion of a terminal hydrogen to a bridging hydrogen (Figure 1). The linear derivative $\text{H}_2\text{Os}_3(\text{CO})_{12}$ with two terminal hydrogen atoms is obtained as one of the products from the high pressure carbonylation of OsO_4 in the presence of hydrogen³ and has been structurally characterized by X-ray crystallography. Other osmium carbonyl hydrides obtained in this reaction include the mononuclear $\text{H}_2\text{Os}(\text{CO})_4$, the binuclear $\text{H}_2\text{Os}_2(\text{CO})_8$, and the tetranuclear $\text{H}_2\text{Os}_4(\text{CO})_{16}$.

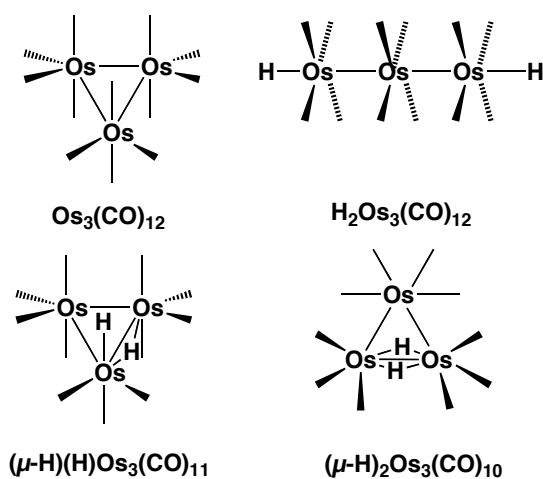


Figure 1. The experimental structures of $\text{Os}_3(\text{CO})_{12}$ and $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 12, 11, 10$). Carbonyl groups are omitted for clarity.

The $\text{Os}_2(\mu\text{-H})_2$ subunit of the $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ structure suggests an analogy with diborane, i. e., $\text{H}_2\text{B}(\mu\text{-H})_2\text{BH}_2$. Similar to diborane, $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ is reactive towards Lewis base ligands, and a variety of substituted $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{10}\text{L}$ derivatives have been obtained by direct reactions of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ with Lewis base ligands.^{4,5,6} Reactions of this type are accompanied by

conversion of one of the bridging hydrogen atoms in $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ into a terminal hydrogen atom with retention of the Os_3 triangle. Such a reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ with CO gives $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{11}$, which has been structurally characterized by X-ray crystallography.⁷ In fact, $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{11}$ is shown to be quasistructural to $\text{Os}_3(\text{CO})_{12}$ with the terminal hydrogen atom replacing one of the CO groups (Figure 1). NMR studies of $(\mu\text{-H})(\text{H})\text{Os}_3(\text{CO})_{11}$ in solution are consistent with this structure but suggest the presence of two minor isomers in ~1% concentration.⁸

This paper presents a theoretical study of these and related trinuclear osmium carbonyl hydrides using density functional methods similar to those used in a previous theoretical study of rhenium carbonyl hydrides.⁹ In addition to the experimentally known $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 12, 11, 10$) systems, the more highly unsaturated $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 9, 8$) are included in this study.

2. Theoretical Methods

Density functional theory (DFT) methods have been employed as a practical and effective computational tool, especially for organometallic complexes.^{10,11,12,13,14,15} In this study, all of the computations were carried out using two selected DFT methods implemented in the Gaussian 09 program suite.¹⁶ The first method is the pure DFT method known as BP86, which combines Becke's 1988 exchange functional with Perdew's 1986 correlation functional.^{17,18} The second method is the MPW1PW91 method.¹⁹ The MPW1PW91 method is a second generation functional²⁰ based on the generalized gradient approximation (GGA), which combines the modified Perdew-Wang exchange functional with the Perdew-Wang 91 gradient-correlation functional.²¹ The BP86 method has been shown to be reliable for first-row transition metal organometallic systems.^{22,23} The MPW1PW91 method has been found to be more suitable for geometry optimization of the second and third row transition metal systems.^{24,25} Normally the BP86 method provides vibrational frequencies, particularly $\nu(\text{CO})$ frequencies, that are closer to experimental values.

The two basis sets used here are the SDD basis set for the Os atom, and the double- ζ plus polarization (DZP) basis sets for the other atoms (C, O, and H). The SDD basis sets combine DZ and Stuttgart-Dresden ECP (relativistic effective core potential) basis sets.²⁶ This can reduce the cost caused by the large numbers of electrons of the third row transition metals. The DZP basis sets for C and O are Huzinaga-Dunning's contracted double- ζ contraction sets^{27,28} 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). For hydrogen, a set of p polarization functions is used with $\alpha_p(\text{H}) = 0.75$. For the osmium carbonyl hydride derivatives $\text{H}_2\text{Os}_3(\text{CO})_{12}$, $\text{H}_2\text{Os}_3(\text{CO})_{11}$, $\text{H}_2\text{Os}_3(\text{CO})_{10}$, $\text{H}_2\text{Os}_3(\text{CO})_9$, and $\text{H}_2\text{Os}_3(\text{CO})_8$ there are 478, 448, 418, 388 and 358 contracted Gaussian basis functions, respectively.

Structures are designated by **a-n**, where **a** is the number of carbonyl groups, **n** orders the structures according to their relative energies for the same spin state by the MPW1PW91 method, respectively. Thus the lowest lying $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structure is designated as **11-1**.

All of the $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 12, 11, 10, 9, 8$) structures obtained in this study are genuine minima with no imaginary vibrational frequencies. Except for the single $\text{H}_2\text{Os}_3(\text{CO})_{12}$ structure **12-1**, all of the $\text{H}_2\text{Os}_3(\text{CO})_n$ structures have a central Os_3 triangle with three osmium-osmium bonds.

3. Results

3.1 $\text{H}_2\text{Os}_3(\text{CO})_{12}$

The only $\text{H}_2\text{Os}_3(\text{CO})_{12}$ structure found in this study is the known D_{4h} structure **12-1** with 12 terminal CO groups and two terminal hydrogen atoms (Figure 2). This D_{4h} structure is a genuine minimum. The Os–Os bond distances of 2.957 Å (MPW1PW91) or 3.006 Å (BP86) correspond to the expected formal single bonds to give each Os atom the favored 18-electron configuration. The twelve predicted $\nu(\text{CO})$ frequencies of the terminal CO groups for structure **12-1** range from 1964 to 2113 cm^{-1} . The two $\nu(\text{OsH})$ frequencies for the two terminal H atoms are both predicted to be 2055 cm^{-1} and thus are buried in the $\nu(\text{CO})$ frequencies.

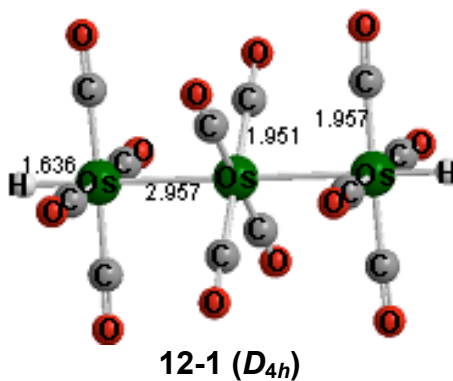


Figure 2. The optimized $\text{H}_2\text{Os}_3(\text{CO})_{12}$ structure predicted by the MPW1PW91 method.

3.2 $\text{H}_2\text{Os}_3(\text{CO})_{11}$

Four singlet $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structures were found within 15 kcal/mol of the lowest energy structure (Figure 3, Table 1). Other higher energy singlet and triplet $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structures are not considered here. These four $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structures lie in a narrow 2 kcal/mol energy range, thus suggesting a fluxional system.⁷

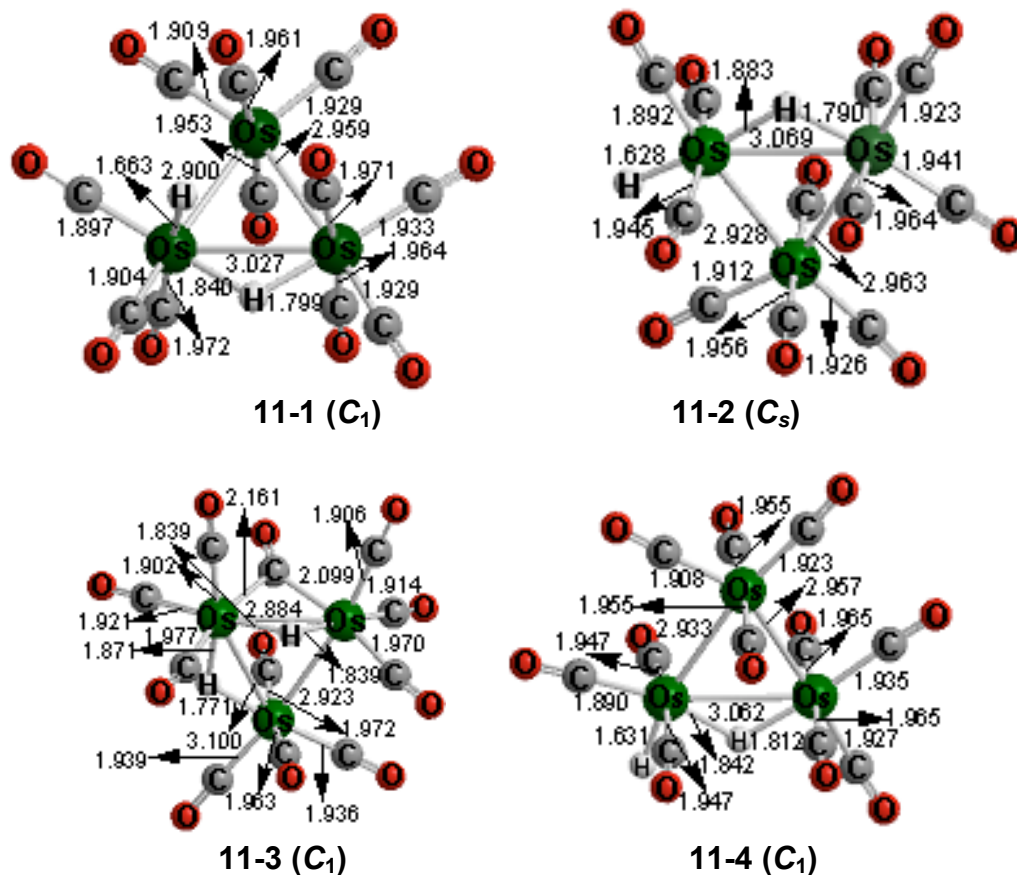


Figure 3. Four optimized structures of $H_2Os_3(CO)_{11}$. Distances are given in Angstroms using the MPW1PW91 method.

Table 1: Total energies (E in hartree), relative energies (ΔE in kcal/mol), and $H\cdots H$ distances ($r_{H\cdots H}$ in Å) of the four $H_2Os_3(CO)_{11}$ equilibrium geometries.

	MPW1PW91			BP86			expt ^a
	E	ΔE	$r_{H\cdots H}$	E	ΔE	$r_{H\cdots H}$	$r_{H\cdots H}$
11-1 (C_1)	-1520.3421441	0.0	2.415	-1521.0455724	0.0	2.406	2.46 ± 0.04
11-2 (C_s)	-1520.3404790	1.0	3.506	-1521.0450386	0.3	3.527	3.34 ± 0.07
11-3 (C_1)	-1520.3402649	1.2	2.871	-1521.0452362	0.2	2.882	—
11-4 (C_1)	-1520.3389362	2.0	2.082	-1521.0431104	1.5	2.067	2.12 ± 0.06

^aThese experimental $H\cdots H$ distances were determined by proton NMR T_1 measurements.⁸

The global minimum $H_2Os_3(CO)_{11}$ structure **11-1** has one bridging hydrogen atom, one terminal hydrogen atom, and eleven terminal carbonyl groups (Figure 3 and Table 1). The three Os–Os distances in **11-1** of 2.900, 2.959, and 3.027 Å (MPW1PW91) are slightly longer than the

experimental Os-Os distances of 2.8574, 2.9097 and 2.9886 Å, determined by single crystal X-ray structural analysis.⁷ They correspond to formal single bonds. The longest Os-Os single bond is the one bridged by the hydrogen atom in accord with the experimental structure. The terminal hydrogen atom in **11-1** is nearly perpendicular to the plane of the Os₃ triangle with a predicted angle between the Os-H vector and the Os₃ plane of 83.1° (MPW1PW91) or 83.0° (BP86). The eleven predicted $\nu(\text{CO})$ frequencies for the terminal CO groups in **11-1** range from 1942 to 2106 cm⁻¹ by the BP86 method. The three predicted $\nu(\text{OsH})$ frequencies for **11-1** are 1251, 1498, and 2053 cm⁻¹. The two relatively low $\nu(\text{OsH})$ frequencies correspond to the Os-H bonds to the bridging hydrogen atom whereas the higher $\nu(\text{OsH})$ frequency corresponds to the Os-H bond to the terminal hydrogen atom. Experimentally observed values (KBr pellet) are 1525 cm⁻¹ for the higher $\nu(\text{OsH})$ frequency of the bridging hydrogen and 1930 cm⁻¹ for the terminal $\nu(\text{OsH})$ frequency.⁷

The H₂Os₃(CO)₁₁ structure **11-4**, lying 2.0 kcal/mol (MPW1PW91) or 1.5 kcal/mol (BP86) above **11-1**, can be derived from **11-1** by interchanging the terminal hydrogen atom with a CO group on the same osmium atom (Figure 2 and Table 1). The terminal hydrogen atom in **11-4** is thus coplanar with the Os₃ triangle. Interchanging the terminal hydrogen atom and a terminal CO group in going from **11-1** to **11-4** has relatively little effect on the Os-Os distances in the Os₃ triangle. Thus in **11-4** the Os-Os distances of 2.933, 2.957, and 3.062 Å (MPW1PW91) are within 0.05 Å of those in **11-1**.

The H₂Os₃(CO)₁₁ structures **11-2** and **11-3** lie within 0.2 kcal/mol of energy of each other (Table 1). The C_s structure **11-2** lies only 1.0 kcal/mol (MPW1PW91) or 0.3 kcal/mol (BP86) above the lowest energy H₂Os₃(CO)₁₁ structure **11-1**. In **11-2** all of the CO groups are terminal CO groups and the terminal hydrogen is *trans* to the bridging hydrogen. The H₂Os₃(CO)₁₁ structure **11-3**, lying 1.2 kcal/mol (MPW1PW91) or 0.2 kcal/mol (BP86) above **11-1**, differs from the other low-energy H₂Os₃(CO)₁₁ structures in having two bridging hydrogen atoms and a bridging CO group. The Os-Os bond lengths in **11-3** are 3.100, 2.923, and 2.884 Å (MPW1PW91) or 3.138, 2.968 and 2.919 Å (BP86), suggesting three formal single bonds. The shortest of these single bonds is the one bridged by both the CO group and a hydrogen atom. The low $\nu(\text{CO})$ frequency of 1786 cm⁻¹ in **11-3** corresponds to the bridging carbonyl group. The other $\nu(\text{CO})$ frequencies, ranging from 1976 to 2101 cm⁻¹, correspond to the ten terminal carbonyl groups. The $\nu(\text{OsH})$ frequencies in **11-3** are clearly in the bridging region, ranging from 1159 to 1591 cm⁻¹.

The variable temperature proton NMR of H₂Os₃(CO)₁₁ in toluene-d₈ solution confirms the expected fluxional nature of this system.⁸ One major isomer (~98%) and two minor isomers (~1% each) are found in such solutions. The hydrogen-hydrogen distances ($r_{\text{H}\dots\text{H}}$ in Table 1) of each isomer were deduced from proton T_1 measurements at variable temperature. The major isomer is **11-1** corresponding to the H₂Os₃(CO)₁₁ structurally characterized by X-ray crystallography.⁷ The $r_{\text{H}\dots\text{H}}$ for **11-1** of ~2.41 Å predicted by both MPW1PW91 and BP86 is in essential agreement with

the experimental value of 2.46 ± 0.04 Å. Comparison of experimental $r_{\text{H}\dots\text{H}}$ values for the two minor $\text{H}_2\text{Os}_3(\text{CO})_{11}$ isomers with the predicted values for the remaining low-energy $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structures identifies the minor isomers as **11-2** and **11-4** (Table 1). Note that the three $\text{H}_2\text{Os}_3(\text{CO})_{11}$ isomers observed experimentally all have one terminal hydrogen, one bridging hydrogen, and all terminal CO groups. The remaining low energy $\text{H}_2\text{Os}_3(\text{CO})_{11}$ isomer **11-3**, with two bridging hydrogens and one bridging CO group, has not yet been observed experimentally.

3.3 $\text{H}_2\text{Os}_3(\text{CO})_{10}$.

Only two singlet structures are found for $\text{H}_2\text{Os}_3(\text{CO})_{10}$ within 15 kcal/mol of the global minimum (Figure 4 and Table 2). The global minimum **10-1** exhibits C_{2v} symmetry with ten terminal CO groups and two equivalent hydrogen atoms bridging the same Os=Os edge. This predicted geometry of **10-1** agrees well with the experimental structure determined by X-ray crystallography. Thus the predicted Os-Os bond distances of 2.715, 2.847, and 2.847 Å (MPW1PW91) or 2.745, 2.886, and 2.886 Å (BP86) agree well with the corresponding experimental Os-Os distances of 2.683, 2.815, and 2.814 Å with the MPW1PW91 distances agreeing better with experiment than the BP86 distances. The short ~ 2.7 Å edge of the Os_3 triangle in **10-1** is the one bridged by the two hydrogen atoms. This central $\text{Os}_2(\mu\text{-H})_2$ unit in **10-1** is analogous to the central $\text{B}_2(\mu\text{-H})_2$ unit in diborane and thus can be regarded as a diprotonated Os=Os double bond. This gives each osmium atom in **10-1** the favored 18-electron configuration. The terminal $\nu(\text{CO})$ frequencies are in the expected region, ranging from 1976 to 2084 cm^{-1} . The $\nu(\text{OsH})$ frequencies of 1461, 1417, 1258, and 1249 cm^{-1} in **10-1** are in the typical region for Os-H bonds to bridging hydrogen atoms.

The experimentally known $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure **10-1** is clearly the most favorable structure since the next lowest energy $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure **10-2** lies 11.9 kcal/mol (MPW1PW91) or 10.3 kcal/mol (BP86) above **10-1** (Figure 4 and Table 2). Structure **10-2**, like **10-1**, has two bridging hydrogen atoms and ten terminal CO groups. The obvious difference between the $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structures **10-1** and **10-2** is that in **10-1** both hydrogen atoms bridge the same Os-Os edge, whereas in **10-2** each hydrogen atom bridges a different Os-Os edge. The predicted Os-Os bond distances in **10-2** are 2.660, 2.860, and 3.002 Å (MPW1PW91) or 2.694, 2.898, and 3.028 Å (BP86). The shortest Os=Os edge of ~ 2.7 Å can be considered as a formal double bond whereas the two significantly longer Os–Os edges of ~ 2.9 and ~ 3.0 Å correspond to formal single bonds. The longer of these two formal Os–Os single bond edges is the one bridged by a hydrogen atom. One Os=Os double bond and two Os–Os single bonds in the Os_3 triangle combined with two bridging hydrogen atoms gives each osmium atom in **10-2** the favored 18-electron configuration. The predicted $\nu(\text{CO})$ and $\nu(\text{OsH})$ frequencies in **10-2** are similar to those in **10-1**.

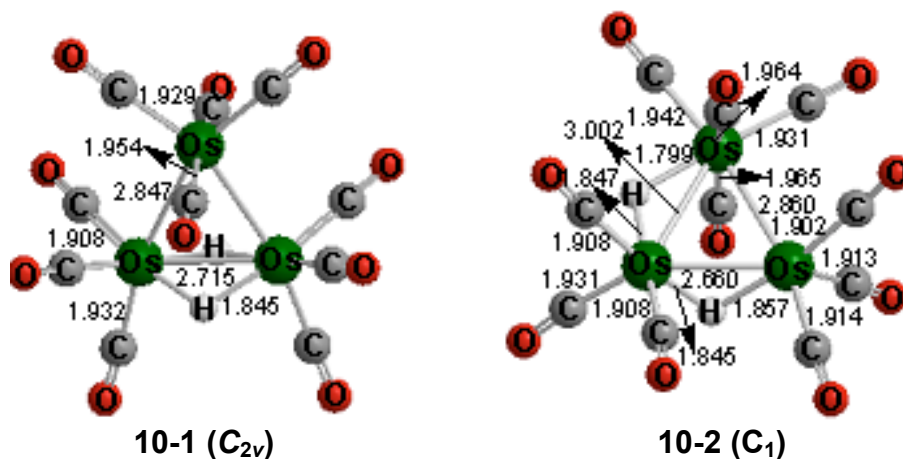


Figure 4. The two lowest energy $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structures by the MPW1PW91 method.

Table 2: Total energies (E , hartree) and relative energies (ΔE , kcal/mol) of the two $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structures.

	MPW1PW91 (E)	MPW1PW91 (ΔE)	BP86 (E)	BP86 (ΔE)
10-1 (C_{2v})	-1407.019263	0.0	-1407.6887876	0.0
10-2 (C_1)	-1407.000301	11.9	-1407.6726038	10.3

3.4 $\text{H}_2\text{Os}_3(\text{CO})_9$

Four low-lying singlet $\text{H}_2\text{Os}_3(\text{CO})_9$ structures are found within 15 kcal/mol of the global minimum (Figure 5 and Table 3). The $\text{H}_2\text{Os}_3(\text{CO})_9$ global minimum **9-1** has C_s symmetry with nine terminal carbonyl groups and one of the edges of the central Os_3 triangle bridged by both hydrogen atoms. Structure **9-1** can be derived from the lowest energy $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure **10-1** (Figure 4) by removing a terminal carbonyl group from the $\text{Os}(\text{CO})_4$ moiety. Removal of this terminal carbonyl group from the $\text{Os}(\text{CO})_4$ moiety in **10-1** shortens the $\text{Os}-\text{Os}$ distance from ~ 2.85 Å in **10-1** to ~ 2.75 Å in **9-1**. Thus the three $\text{Os}-\text{Os}$ bond distances in **9-1** are all similar at 2.748, 2.748, and 2.713 Å (MPW1PW91) or 2.782, 2.782, and 2.737 Å (BP86). The predicted terminal $\nu(\text{CO})$ frequencies in **9-1** range from 1957 to 2071 cm^{-1} .

Table 3. Total energies (E , hartree) and relative energies (ΔE , kcal/mol) of the $\text{H}_2\text{Os}_3(\text{CO})_9$ structures within 15 kcal/mol of the global minimum.

	MPW1PW91 (E)	MPW1PW91 (ΔE)	BP86 (E)	BP86 (ΔE)
9-1 (C_s)	-1293.643544	0.0	-1294.283123	0.0
9-2 (C_1)	-1293.634630	5.6	-1294.279597	2.3
9-3 (C_1)	-1293.628413	9.5	-1294.272382	6.8
9-4 (C_1)	-1293.622693	13.1	-1294.268161	9.5

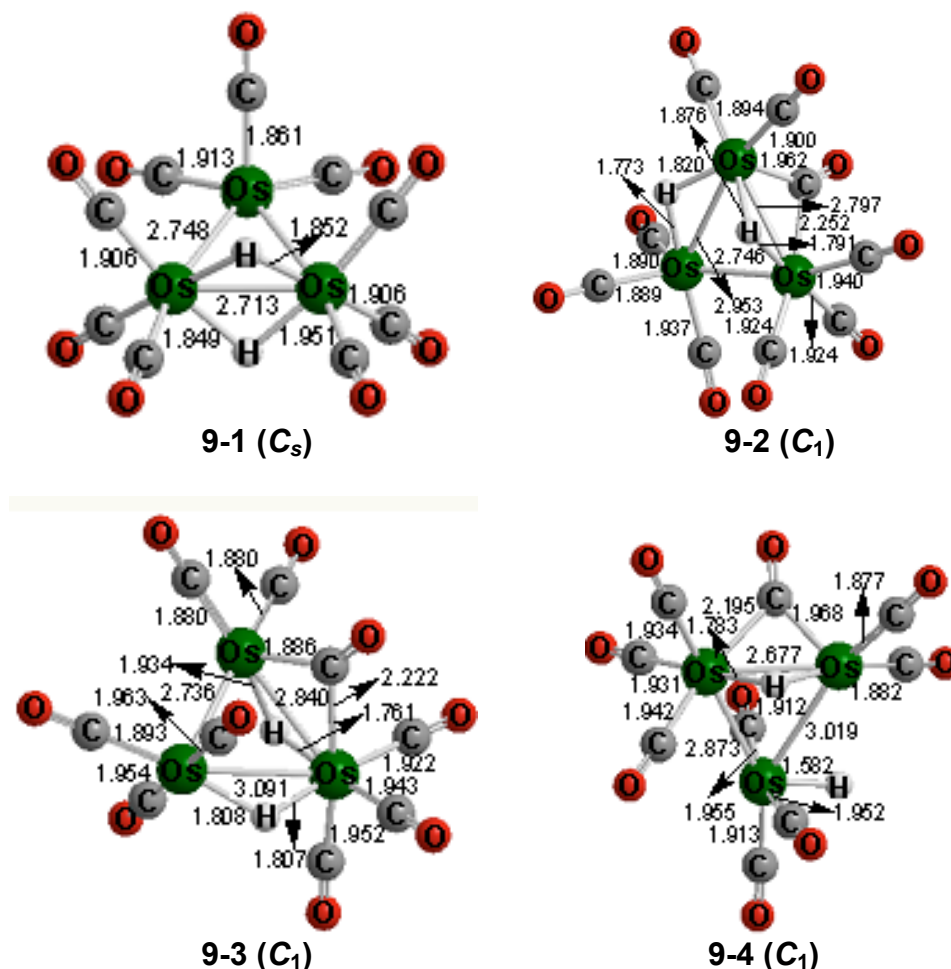


Figure 5. Four optimized $H_2Os_3(CO)_9$ structures within 10 kcal/mol of the global minimum.

The next low energy singlet $H_2Os_3(CO)_9$ structure is the C_1 structure **9-2**, lying only 5.6 kcal/mol (MPW1PW91) or 2.3 kcal/mol (BP86) above **9-1** (Figure 5, Table 3). In **9-2** one of the Os–Os edges of length 2.797 Å (MPW1PW91) or 2.826 Å (BP86) is bridged by both a carbonyl group and a hydrogen atom. This doubly bridged Os–Os edge can be regarded as a formal single bond. Another Os–Os edge of length 2.953 Å (MPW1PW91) or 2.969 Å (BP86) is bridged by the other hydrogen atom. This singly bridged Os–Os edge can likewise be regarded as a formal single bond, which is longer than the doubly bridged likewise formal Os–Os single bond because of the bond shortening effect of bridging groups. The unbridged Os=Os edge of length 2.746 Å (MPW1PW91) or 2.771 Å (BP86) in **9-2** can be regarded as a formal double bond. The predicted $\nu(CO)$ frequencies range from 1839 to 2070 cm^{-1} , among which the lowest $\nu(CO)$ frequency

corresponds to the bridging carbonyl group. The predicted $\nu(\text{OsH})$ frequencies for **9-2** ranging from 1585 to 1116 cm^{-1} are clearly in the bridging hydride region.

The $\text{H}_2\text{Os}_3(\text{CO})_9$ structure **9-3**, lying 9.5 kcal/mol (MPW1PW91) or 6.8 kcal/mol (BP86) above **9-1**, is similar to **9-2** in that one Os–Os edge is bridged by a carbonyl group and a hydrogen atom and another Os–Os edge is bridged by the second hydrogen atom (Figure 5 and Table 3). The two structures **9-2** and **9-3** differ in the arrangement of the eight terminal carbonyl groups around the central $\text{Os}_3(\mu\text{-H})_2(\mu\text{-CO})$ unit. In **9-3** the doubly bridged edge of length 2.840 Å (MPW1PW91) or 2.868 Å (BP86) and singly bridged edge of length 3.091 Å (MPW1PW91) or 3.115 Å (BP86) can clearly be considered as formal single bonds. However, the unbridged Os=Os edge in **9-3** is significantly shorter at 2.736 Å (MPW1PW91) or 2.759 Å (BP86) and thus may be considered a formal double bond. The predicted $\nu(\text{CO})$ frequencies in **9-3** range from 1812 to 2088 cm^{-1} , among which the lowest $\nu(\text{CO})$ frequency corresponds to the bridging carbonyl group. The predicted $\nu(\text{OsH})$ frequencies ranging from 1565 to 1279 cm^{-1} are in the region for bridging hydrogen atoms.

The fourth $\text{H}_2\text{Os}_3(\text{CO})_9$ structure **9-4**, lying 13.1 kcal/mol (MPW1PW91) or 9.5 kcal/mol (BP86) above **9-1**, has one terminal hydrogen, one bridging hydrogen, and one bridging CO group (Figure 5 and Table 3). One of the Os–Os edges is bridged by both the hydrogen atom and carbonyl group and is relatively short at 2.677 Å (MPW1PW91) or 2.691 Å (BP86) because of the two bridging groups. The unbridged Os–Os edges are significantly longer at 2.873 and 3.019 Å (MPW1PW91) or 2.899 and 3.027 Å (BP86) and thus suggest formal single bonds. The osmium atom in **9-4** bearing the terminal hydrogen has a gap in its coordination sphere *trans* to the terminal hydrogen and thus may be assumed to have a 16-electron configuration. In addition, the osmium atom bearing only two terminal carbonyl groups has a gap in its coordination sphere *trans* to the bridging carbonyl group and thus likewise can be assumed to have a 16-electron configuration. The remaining osmium atom in **9-4** appears to have the favored 18-electron configuration. The predicted $\nu(\text{CO})$ frequencies range from 1834 to 2076 cm^{-1} with the 1834 cm^{-1} frequency corresponding to the bridging carbonyl group. The predicted $\nu(\text{OsH})$ frequencies for **9-4** range from 1167 to 2245 cm^{-1} with the 2245 cm^{-1} frequency corresponding to the terminal hydrogen.

3.5 $\text{H}_2\text{Os}_3(\text{CO})_8$

Six structures were found for $\text{H}_2\text{Os}_3(\text{CO})_8$ within 11 kcal/mol of the global minimum (Figure 6, Table 4). The global minimum $\text{H}_2\text{Os}_3(\text{CO})_8$ structure **8-1** has C_1 symmetry and is derived from the lowest energy $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure **10-1** by removing carbonyl groups from one $\text{Os}(\text{CO})_4$ unit and from one $\text{Os}(\text{CO})_3$ unit. Removal of these carbonyl groups shortens one of the unbridged Os=Os distances in **8-1** to 2.586 Å (MPW1PW91) or 2.596 Å (BP86), which can be interpreted as a formal triple bond. The doubly hydrogen bridged edge in **8-1** of length 2.665 Å

(MPW1PW91) or 2.680 Å (BP86) is ~ 0.05 Å shorter than the diprotonated Os=Os double bond in **9-1** but likewise can be interpreted as a diprotonated Os=Os double bond. The remaining unbridged Os–Os edge of length 2.789 Å (MPW1PW91) or 2.831 Å (BP86) in **8-1** can correspond to a formal single bond. By using this interpretation of the Os–Os bonding in the Os₃ triangle of **8-1**, all of the Os atoms are found to have the favored 18-electron configuration. The predicted $\nu(\text{CO})$ frequencies for **8-1** range from 1965 to 2066 cm^{-1} in the typical terminal carbonyl region. The predicted $\nu(\text{OsH})$ frequencies for structure **8-1** range from 1497 to 1205 cm^{-1} in the bridging hydride region.

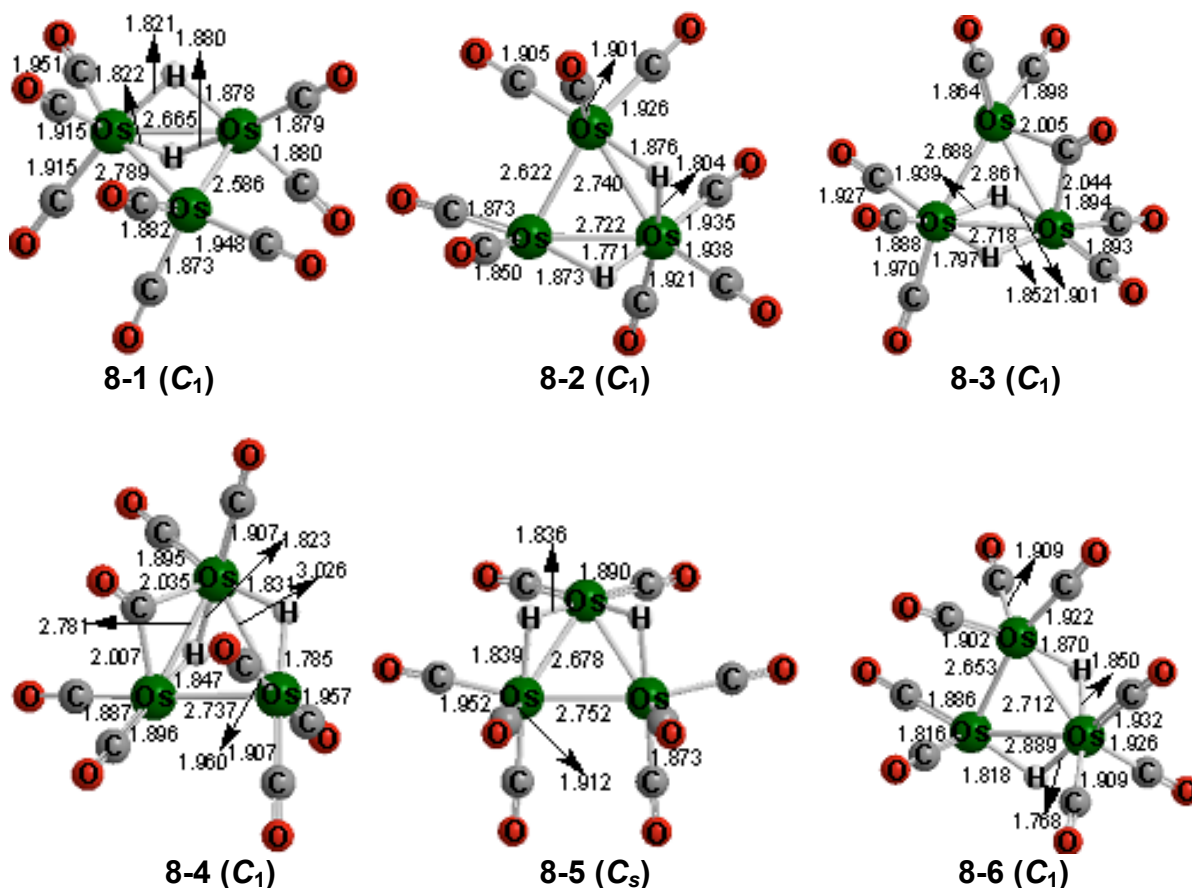


Figure 6. Six optimized singlet $\text{H}_2\text{Os}_3(\text{CO})_8$ structures.

The $\text{H}_2\text{Os}_3(\text{CO})_8$ structure **8-2**, lying 3.4 kcal/mol (MPW1PW91) or 3.1 kcal/mol (BP86) above **8-1**, has two bridging hydrogen atoms and all terminal carbonyl groups like **8-1** (Figure 6 and Table 4). The three Os–Os edges in the Os₃ triangle of **8-2** of lengths 2.622, 2.722, and 2.740 Å (MPW1PW91) or 2.637, 2.727, and 2.784 Å (BP86) appear to be multiple bonds. The osmium atom bonded to only two terminal carbonyl groups in **8-2** has a gap in its coordination sphere *trans* to the Os–Os bond and thus appears to have a 16-electron configuration.

Table 4. Total energies (E, hartree) and relative energies (ΔE , kcal/mol) of the six $\text{H}_2\text{Os}_3(\text{CO})_8$ structures.

	MPW1PW91 (E)	MPW1PW91 (ΔE)	BP86 (E)	BP86 (ΔE)
8-1 (C_1)	-1180.286587	0	-1180.895883	0
8-2 (C_1)	-1180.281151	3.4	-1180.890967	3.1
8-3 (C_1)	-1180.271422	9.5	-1180.884189	7.3
8-4 (C_1)	-1180.270545	10.1	-1180.883302	7.9
8-5 (C_s)	-1180.270091	10.4	-1180.880553	9.6
8-6 (C_1)	-1180.269763	10.6	-1180.879923	10.0

The $\text{H}_2\text{Os}_3(\text{CO})_8$ structure **8-3**, lying 9.5 kcal/mol (MPW1PW91) or 7.3 kcal/mol (BP86) in energy above **8-1**, has an Os=Os edge of length 2.718 Å (MPW1PW91) or 2.752 Å (BP86) bridged by the two hydrogen atoms as well as a carbonyl group bridging a different Os-Os edge (Figure 6 and Table 4). Structure **8-3** thus can be derived from the lowest energy $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure **10-1** (Figure 4) by removal of two carbonyl groups from the $\text{Os}(\text{CO})_4$ moiety, followed by bridging one of the terminal carbonyl groups from one of the other osmium atoms to the original $\text{Os}(\text{CO})_4$ osmium atom. The unbridged Os=Os edge in **8-3** is relatively short at 2.688 Å (MPW1PW91) or 2.710 Å (BP86) and thus can correspond to a formal double bond. The remaining Os–Os edge in **8-3**, i. e., the edge bridged by the carbonyl group, of length 2.861 Å (MPW1PW91) or 2.866 Å (BP86) corresponds to a formal single bond. This gives each osmium atom in the $\text{Os}_2(\mu\text{-H})_2$ unit the favored 18-electron configuration but the remaining osmium atom only a 16-electron configuration consistent with an apparent gap in its coordination sphere.

The $\text{H}_2\text{Os}_3(\text{CO})_8$ structure **8-4**, lying 10.1 kcal/mol (MPW1PW91) or 7.9 kcal/mol (BP86) above **8-1**, has one Os–Os edge is bridged by a carbonyl group and a hydrogen atom and another Os–Os edge bridged by the second hydrogen atom (Figure 6 and Table 4). Structure **8-4** can be derived from **9-3** (Figure 5) by removal of a terminal CO group. Removal of the terminal CO group from **9-3** to give **8-4** has relatively little effect on the Os-Os distances in the central Os_3 triangle, so that similar interpretations of the Os-Os bonding apply to both structures.

The fifth $\text{H}_2\text{Os}_3(\text{CO})_8$ structure **8-5**, of C_s symmetry and lying 10.4 kcal/mol (MPW1PW91) or 9.6 kcal/mol (BP86) in energy above **8-1**, has two equivalent Os=Os edges of length 2.678 Å (MPW1PW91) or 2.697 Å (BP86) bridged by hydrogen atoms and an unbridged Os=Os edge of length 2.752 Å (MPW1PW91) or 2.792 Å (BP86) (Figure 6 and Table 4). All of these Os=Os edges can be interpreted as formal double bonds. This gives the equivalent osmium atoms bearing three carbonyl groups in **8-5** the favored 18-electron configuration but the unique osmium atom only a 16-electron configuration.

The $\text{H}_2\text{Os}_3(\text{CO})_8$ structure **8-6**, lying 10.6 kcal/mol (MPW1PW91) or 10.0 kcal/mol (BP86) in energy above **8-1**, is similar to **8-2** except for a different orientation of the carbonyl groups.

3.6 Thermochemistry

Table 5 lists the carbonyl dissociation energies for the trinuclear osmium carbonyl hydrides, based on the lowest energy structures. The carbonyl dissociation energies of both $\text{H}_2\text{Os}_3(\text{CO})_{12}$ and $\text{H}_2\text{Os}_3(\text{CO})_{11}$ of ~ 20 kcal/mol are significant, consistent with the fact that under ambient conditions both are stable compounds that have been characterized structurally. However, these carbonyl dissociation energies are significantly lower than the experimental carbonyl dissociation energies of 27 kcal/mol, 41 kcal/mol, and 37 kcal/mol for $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$, respectively.²⁹ The carbonyl dissociation energy of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ of ~ 50 kcal/mol is significantly higher than that of either $\text{H}_2\text{Os}_3(\text{CO})_{12}$ or $\text{H}_2\text{Os}_3(\text{CO})_{11}$, consistent with the fact that it is the product obtained from reaction of $\text{Os}_3(\text{CO})_{12}$ with hydrogen at elevated temperatures.

Table 5. Dissociation energies (kcal/mol) for successive removal of carbonyls from $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 12, 11, 10, 9$)

	MPW1PW91	BP86
$\text{H}_2\text{Os}_3(\text{CO})_{12} \rightarrow \text{H}_2\text{Os}_3(\text{CO})_{11} + \text{CO}$	20.1	21.4
$\text{H}_2\text{Os}_3(\text{CO})_{11} \rightarrow \text{H}_2\text{Os}_3(\text{CO})_{10} + \text{CO}$	17.6	18.5
$\text{H}_2\text{Os}_3(\text{CO})_{10} \rightarrow \text{H}_2\text{Os}_3(\text{CO})_9 + \text{CO}$	51.4	48.8
$\text{H}_2\text{Os}_3(\text{CO})_9 \rightarrow \text{H}_2\text{Os}_3(\text{CO})_8 + \text{CO}$	38.4	38.1

The disproportionation energies for the reactions $2\text{H}_2\text{Os}_3(\text{CO})_n \rightarrow \text{H}_2\text{Os}_3(\text{CO})_{n+1} + \text{H}_2\text{Os}_3(\text{CO})_{n-1}$ were also determined (Table 6). The disproportionation of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ into $\text{H}_2\text{Os}_3(\text{CO})_{11} + \text{H}_2\text{Os}_3(\text{CO})_9$ is highly endothermic at ~ 30 kcal/mol suggesting that it is the thermodynamic sink in the $\text{H}_2\text{Os}_3(\text{CO})_n$ system, again consistent with its synthesis from $\text{Os}_3(\text{CO})_{12}$ and H_2 at elevated temperatures. On the other hand, the disproportionation of $\text{H}_2\text{Os}_3(\text{CO})_9$ into $\text{H}_2\text{Os}_3(\text{CO})_{10} + \text{H}_2\text{Os}_3(\text{CO})_8$ is exothermic, consistent with the fact that $\text{H}_2\text{Os}_3(\text{CO})_9$ is unknown unlike the carbonyl-richer species $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 12, 11, 10$).

Table 6. Energies (kcal/mol) for the disproportionation reactions $2\text{H}_2\text{Os}_3(\text{CO})_n \rightarrow \text{H}_2\text{Os}_3(\text{CO})_{n+1} + \text{H}_2\text{Os}_3(\text{CO})_{n-1}$. All of the energies refer to the lowest energy structures of $\text{H}_2\text{Os}_3(\text{CO})_n$ without zero-point energy corrections.

	MPW1PW91	BP86
$2\text{H}_2\text{Os}_3(\text{CO})_{11} \rightarrow \text{H}_2\text{Os}_3(\text{CO})_{12} + \text{H}_2\text{Os}_3(\text{CO})_{10}$	2.5	2.9
$2\text{H}_2\text{Os}_3(\text{CO})_{10} \rightarrow \text{H}_2\text{Os}_3(\text{CO})_{11} + \text{H}_2\text{Os}_3(\text{CO})_9$	33.8	30.2
$2\text{H}_2\text{Os}_3(\text{CO})_9 \rightarrow \text{H}_2\text{Os}_3(\text{CO})_{10} + \text{H}_2\text{Os}_3(\text{CO})_8$	-13.0	-0.7

4. Discussion

Only one $\text{H}_2\text{Os}_3(\text{CO})_{12}$ structure is predicted here at accessible energies, namely the linear structure **12-1** with all terminal carbonyl and hydride ligands and two Os–Os single bonds. This species is known experimentally and is a member of the homologous series $\text{H}_2[\text{Os}(\text{CO})_4]_n$ of linear structures ($n = 1, 2, 3$).³ All three osmium atoms have the favored 18-electron configuration in structure **12-1**.

The $\text{H}_2\text{Os}_3(\text{CO})_{12}$ structure **12-1** is the only $\text{H}_2\text{Os}_3(\text{CO})_n$ structure found in this work in which both hydride ligands are terminal ligands. All of the $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 11, 10, 9$) structures found in this work have a triangular rather than a linear arrangement of the three osmium atoms and at least one edge-bridging $\mu\text{-H}$ ligand. However, no $\text{H}_2\text{Os}_3(\text{CO})_n$ structures with $\mu_3\text{-H}$ ligands bridging all three osmium atoms of the Os_3 triangle are found, in contrast to our previous study of trinuclear rhenium carbonyl hydrides $\text{H}_3\text{Re}_3(\text{CO})_n$ ($n = 12, 11, 10, 9$).⁹ None of the low-energy $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 11, 10$) structures have bridging carbonyl groups.

The $\text{H}_2\text{Os}_3(\text{CO})_{11}$ energy surface is more complicated than the $\text{H}_2\text{Os}_3(\text{CO})_{12}$ energy surface since the four lowest energy structures lie within ~ 2 kcal/mol of each other. Three of the four lowest energy $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structures, namely **11-1**, **11-2**, and **11-4**, have one terminal hydride and one bridging hydride and are differentiated by the position of the terminal hydride relative to the central $\text{Os}_3(\mu\text{-H})$ unit. This is also reflected in very different non-bonding $\text{H}\cdots\text{H}$ distances for the three structures (Table 1). The lowest energy of these three $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structures **11-1** has been synthesized and structurally characterized by X-ray crystallography.⁷ As is typical for hydrides of heavy transition metals, the hydrogen atoms were not located in the experimental X-ray structure. However, this $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structure appears to be isomorphic with $\text{Os}_3(\text{CO})_{12}$ with the terminal hydride ligand occupying the position of the twelfth carbonyl group.

The close spacing of the energies of the four $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structures suggests a fluxional system, which has been studied by variable temperature NMR.⁸ Proton T_1 measurements from this NMR study provide a means of deducing the non-bonding $\text{H}\cdots\text{H}$ distance in the $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structure **11-1**, which is not available from the X-ray crystallographic study. In this connection, the predicted $\text{H}\cdots\text{H}$ distance of 2.415 Å from our theoretical study is essentially identical to the experimental $\text{H}\cdots\text{H}$ distance of 2.46 ± 0.04 Å (Table 1). The proton NMR study also revealed two minor $\text{H}_2\text{Os}_3(\text{CO})_{11}$ isomers present to the extent of $\sim 1\%$ in the toluene- d_8 solution of $\text{H}_2\text{Os}_3(\text{CO})_{11}$. Comparison of their experimental $\text{H}\cdots\text{H}$ distances from proton T_1 measurements with our predicted $\text{H}\cdots\text{H}$ distances identifies these minor isomers as **11-2** and **11-4** (Table 1).

The product obtained from reaction of $\text{Os}_3(\text{CO})_{12}$ with H_2 under relatively harsh conditions (120°C in boiling octane) is the decacarbonyl $\text{H}_2\text{Os}_3(\text{CO})_{10}$ **10-1**, which has a short Os=Os doubly bonded edge bridged by both hydrogen atoms. This observation of the $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure **10-1**

as an apparent thermodynamic “sink” in the trinuclear osmium carbonyl hydride system is identified in our theoretical work in the following ways:

- (1) The $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure **10-1** is the lowest energy $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure by more than 10 kcal/mol (Table 2);
- (2) The predicted CO dissociation energy of $\text{H}_2\text{Os}_3(\text{CO})_{11}$ to give $\text{H}_2\text{Os}_3(\text{CO})_{10}$ is only ~18 kcal/mol whereas that for CO dissociation from $\text{H}_2\text{Os}_3(\text{CO})_{10}$ to give $\text{H}_2\text{Os}_3(\text{CO})_9$ is much higher at ~50 kcal/mol (Table 5).

The doubly bridged $\text{Os}_2(\mu\text{-H})_2$ edge in the $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure **10-1** is completely analogous to the central $\text{B}_2(\mu\text{-H})_2$ unit in diborane and can be considered to be a diprotonated double bond. Such a diprotonated $(\text{Os}=\text{Os})(\mu\text{-H})_2$ double bond effectively contributes three electrons to each osmium atom so that each osmium atom in the $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure **10-1** has the favored 18-electron configuration. Thus, although $\text{H}_2\text{Os}_3(\text{CO})_{10}$ is thermally stable enough to be produced at relatively high temperatures from $\text{Os}_3(\text{CO})_{12}$ and H_2 , it also has Lewis acidic properties like diborane. Extensive series of trinuclear osmium carbonyl derivatives have been prepared by reactions of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with diverse Lewis bases and other types of ligands.^{4,5,6,30}

The lowest energy structures of the decarbonylation products of $\text{H}_2\text{Os}_3(\text{CO})_{10}$, namely the $\text{H}_2\text{Os}_3(\text{CO})_9$ structure **9-1** and the $\text{H}_2\text{Os}_3(\text{CO})_8$ structure **8-1**, are derived from the $\text{H}_2\text{Os}_3(\text{CO})_{10}$ structure **10-1** by loss of one or two CO groups, respectively, while maintaining the central $\text{Os}_3(\mu\text{-H})_2$ unit. Thus one and two osmium atoms in these structures, respectively, have only 16-electron configurations. The higher energy $\text{H}_2\text{Os}_3(\text{CO})_n$ structures ($n = 9, 8$) also have two bridging hydrogen atoms, but not necessarily bridging the same Os–Os edge. Bridging carbonyl groups are also found in some of the $\text{H}_2\text{Os}_3(\text{CO})_n$ structures ($n = 9, 8$) including the $\text{H}_2\text{Os}_3(\text{CO})_9$ structures **9-2**, **9-3**, and **9-4** and the $\text{H}_2\text{Os}_3(\text{CO})_8$ structures **8-3** and **8-4**.

5. Summary

The only low energy $\text{H}_2\text{Os}_3(\text{CO})_{12}$ structure has a linear Os–Os–Os unit with a terminal hydrogen at each end and four terminal CO groups on each osmium atom. However, all of the $\text{H}_2\text{Os}_3(\text{CO})_n$ structures ($n = 11, 10, 9$) have a central Os_3 triangle. For $\text{H}_2\text{Os}_3(\text{CO})_{11}$, four structures are found within ~2 kcal/mol in energy suggesting a fluxional system. Three of these four $\text{H}_2\text{Os}_3(\text{CO})_{11}$ structures have one terminal and one bridging hydrogen atom and have been observed experimentally by NMR. The lowest energy of these three structures is the dominant structure in solution and has been isolated and structurally characterized by X-ray crystallography.

The thermochemistry of the $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 12, 11, 10, 9, 8$) systems suggests that the thermodynamic sink is the $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ structure in which a short Os=Os edge of the Os_3 triangle is bridged by both hydrogen atoms. This species is readily obtained by reaction of

$\text{Os}_3(\text{CO})_{12}$ with hydrogen at elevated temperatures (e.g., 120°C in boiling octane) and is a precursor to numerous trinuclear osmium carbonyl hydride derivatives. The lowest energy structures of the more highly unsaturated $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 9, 8$) can be derived from this $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ structure by removal of CO groups from the osmium atom remote to the doubly bridged Os=Os edge of the Os_3 triangle.

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Supporting Information. Tables S1 to S5: Theoretical harmonic vibrational frequencies (in cm^{-1}) for the $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 12, 11, 10, 9, 8$) structures by the BP86/SDD method; Tables S6 to S22: Optimized Cartesian coordinates (in Å) for the $\text{H}_2\text{Os}_3(\text{CO})_n$ ($n = 12, 11, 10, 9, 8$) structures using the MPW1PW91/SDD method; Complete Gaussian 09 reference.

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