Binuclear Cyclopentadienylmetal Carbonyl Hydrides of Iridium, Osmium, and Rhenium: The Effect of Electron Count on the Preferred Structures

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Abstract

The $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}; n = 3, 2, 1$) systems, related to the experimentally known and structurally characterized permethylated derivatives $\text{Cp}^*_2\text{M}_2\text{H}_2(\text{CO})_2$ ($\text{Cp}^* = \eta^5\text{-Me}_5\text{C}_5$; $\text{M} = \text{Ir}, \text{Os}$), provide examples of binuclear structures having metal-metal bonds of formal orders ranging from zero to four as determined by the 18-electron rule. The low-energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structures lacking a direct iridium-iridium bond necessarily have a bridging CO group holding together the two iridium atoms. For $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$, low-energy unbridged structures are found corresponding to the experimental unbridged $\text{Cp}^*_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure. However, for $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ the lowest energy structure has two hydrogen atoms bridging the formal $\text{Os}=\text{Os}$ double bond similar to the experimental doubly bridged $\text{Cp}^*_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure. The lowest energy structures of the monocarbonyls $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})$ have all three ligands ($2\text{H} + \text{CO}$) bridging a central metal-metal bond. The $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structures provide examples of both bridged and unbridged structures containing formal Re-Re quadruple bonds with highly bridged structures being preferred energetically.

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1. Introduction

Hydrides of the third row transition metals are found to be more stable and correspondingly less reactive than those of the first and second row transition metals. For example, rhenium forms the unusual stable binary nonacoordinate anion [1,2] ReH_9^{2-} . Stable cyclopentadienylmetal polyhydrides of the third row transition metals include the mononuclear derivatives Cp^*MH_n ($\text{Cp}^* = \eta^5\text{-Me}_5\text{C}_5$; $\text{M} = \text{Re}$ [3,4], $n = 6$; $\text{M} = \text{Os}$ [5], $n = 5$; $\text{M} = \text{Ir}$ [6], $n = 4$). All of these mononuclear metal hydride derivatives obey the 18-electron rule [7,8,9,10,11]. The stable binuclear derivatives $\text{Cp}^*_2\text{M}_2\text{H}_n$ ($\text{M} = \text{Re}$ [3,4], $n = 6$; $\text{M} = \text{Os}$ [5], $n = 4$; $\text{M} = \text{Ir}$ [12], $n = 2$) also obey the 18-electron rule if the central $\text{M}\equiv\text{M}$ bond is regarded as a formal triple bond. In addition the mononuclear cyclopentadienylmetal carbonyl hydrides $\text{CpW}(\text{CO})_3\text{H}$ [13], $\text{CpRe}(\text{CO})_2\text{H}_2$ [14], $\text{CpOs}(\text{CO})_2\text{H}$ [15], and $\text{Cp}^*\text{Os}(\text{CO})\text{H}_3$ [16] are all isolable compounds, which are more stable and thus correspondingly less reactive than their analogues containing first and second row transition metals.

Two binuclear cyclopentadienylmetal carbonyl hydrides are known containing the third row transition metals, namely $\text{Cp}^*_2\text{Os}_2(\text{CO})_2\text{H}_2$ [16] and $\text{Cp}^*_2\text{Ir}_2(\text{CO})_2\text{H}_2$ [17]. Of interest are the same molecular formulas for both species even though osmium has eight valence electrons and iridium has nine valence electrons. The structures of both species have been partially determined by X-ray crystallography but the hydrogen atoms could not be located. In order to clarify the nature of these species and related binuclear cyclopentadienylmetal carbonyl hydrides, the structures and thermochemistry of the complete series of $\text{Cp}_2\text{M}_2(\text{CO})_n\text{H}_2$ ($\text{M} = \text{Re}, \text{Os}, \text{Ir}$; $n = 3, 2, 1$) have been investigated using density functional theory. The metal-metal interactions in these binuclear cyclopentadienylmetal carbonyl hydrides are of particular interest since species with formal metal-metal bond orders ranging from 0 to 4 are found.

2. Theoretical Methods

Electron correlation effects were considered by employing density functional theory (DFT) methods, which have been regarded as a practical and effective computational tool, especially for organometallic compounds [18,19,20,21,22,23,24]. In our study, three DFT methods were used, namely BP86, MPW1PW91, and M06-L. The BP86 method is a pure DFT method combining Becke's 1988 exchange functional (B) with Perdew's 1986 gradient-corrected correlation functional (P86) [25,26]. The MPW1PW91 method combines the modified Perdew-Wang exchange functional with the Perdew-Wang 91 gradient-correlation functional [27]. The M06-L method developed by Zhao and Truhlar

[28] is based on the M05 [29] and VSXC [30] functionals. The MPW1PW91 functional is better than the first-generation functionals for second- and third-row transition metal systems [31], whereas the BP86 method provides more accurate vibrational frequencies [32,33]. In addition, a recent detailed study of 35 different DFT methods suggests that the M06-L method coupled with suitable basis sets predicts structures very consistent with experiment for transition metal organometallic and carbonyl derivatives [34]. For this reason, only the M06-L results (geometries, energies, and interatomic distances) are discussed in the text unless specifically noted otherwise.

The geometries of the $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Re}, \text{Os}, \text{Ir}; n = 3, 2, 1$) structures were fully optimized using the two selected DFT methods with DZP and SDD basis sets for the light atoms and heavy atoms, respectively. Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. Our DZP basis sets used for carbon, oxygen, and hydrogen add one set of pure spherical harmonic d functions with orbital exponents $R_d(\text{C}) = 0.75$, $R_d(\text{O}) = 0.85$, and $R_d(\text{H}) = 0.70$ to the standard Huzinaga-Dunning-Hay contracted DZ sets [35,36]. The carbon and oxygen basis sets are designated as (9s5p1d/4s2p1d), whereas the hydrogen basis set is designated as (4s1p/2s1p). The Stuttgart-Dresden double- ζ (SDD) effective core potential (ECP) basis set was used for the rhenium, osmium, and iridium atoms [37,38].

All of the computations were carried out using the Gaussian 09 program package [39]. A large number of stable structures were predicted by these three methods. If not specifically mentioned, only those structures with energies within $\sim 10 \text{ kcal}\cdot\text{mol}^{-1}$ by the M06-L method are discussed in the text. A summary of the vibrational frequencies and structure data calculated by M06-L, MPW1PW91 and BP86 method is given in the Supporting Information.

3. Results

All of the structures discussed in this section have two pentahapto $\eta^5\text{-Cp}$ rings bonded to the metal atom and are genuine minima without any imaginary vibrational frequencies. The structures are ordered based on the energies predicted by the M06-L method.

3.1 The $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_n$ ($n = 3, 2, 1$) structures

3.1.1 $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$. Seven low-energy structures were found for $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ (Figure 1). Five of these seven structures, namely **Ir-3CO-2S** through **Ir-3CO-6S**, are related structures having non-bonding $\text{Ir}\cdots\text{Ir}$ distances ranging from 3.63 to 3.76 Å and closely spaced energies ranging from 1.2 to 3.9 $\text{kcal}\cdot\text{mol}^{-1}$ above **Ir-3CO-1S**. Thus the two

halves of each of these five molecules are held together solely by the bridging CO group. All five structures have one terminal hydrogen atom and one terminal CO group on each metal atom and differ only in the relative locations of the ligands.

Figure 1. Optimized geometries of the seven $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structures including the Ir-Ir distances and relative energies.

The remaining two low-energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structures **Ir-3CO-1S** and **Ir-3CO-7S** are geometrically quite different from the five structures **Ir-3CO-2S** through **Ir-3CO-6S**. Structure **Ir-3CO-1S** is the lowest energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structure. In **Ir-3CO-1S** one iridium atom bears a terminal CO group and a terminal hydrogen atom whereas the other iridium atom bears a terminal CO group and a terminal formyl group. Structure **Ir-3CO-7S**, lying $9.5 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-3CO-1S**, is unusual since

one of the Cp rings has “slipped” to become a trihapto ligand rather than the usual pentahapto ligand. The iridium atom bearing the trihapto Cp ring in **Ir-3CO-7S** is bonded to terminal CO groups whereas the other iridium atom is bonded to a terminal hydrogen atom. The third CO group in **Ir-3CO-7S** bridges the two metal atoms. The Ir–Ir distances of ~ 2.8 Å in **Ir-3CO-1S** and **Ir-3CO-7S** can correspond to the formal single bonds required to give each iridium atom the favored 18-electron configuration.

3.1.2 $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$. Nine low-energy singlet $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structures having energies within $9 \text{ kcal}\cdot\text{mol}^{-1}$ were optimized (Figure 2). The Ir–Ir distances in all nine structures are predicted to range from 2.70 to 2.85 Å, consistent with formal single bonds. The global minimum **Ir-2CO-1S** is a C_2 *trans* structure with no bridging CO groups or hydrogen atoms. However, the $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure very close to the experimental $\text{Cp}^*_2\text{Ir}_2\text{H}_2(\text{CO})_2$ ($\text{Cp}^* = \eta^5\text{-Me}_5\text{C}_5$) structure, characterized by X-ray crystallography, is **Ir-2CO-2S**, lying only $0.3 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-2CO-1S** (Table 1) [17]. Thus, the predicted Ir–Ir distance in **Ir-2CO-2S** of 2.779 Å (M06-L), 2.740 Å (MPW1PW91), or 2.769 Å (BP86) is close to the Ir–Ir distance of 2.730 Å for $\text{Cp}^*_2\text{Ir}_2\text{H}_2(\text{CO})_2$ as determined by X-ray crystallography. The predicted Ir–C distances to the terminal CO groups in **Ir-2CO-2S** of 1.834 Å (M06-L), 1.826 Å (MPW1PW91), or 1.833 Å (BP86) are close to the experimental values of 1.817 and 1.829 Å for the two Ir–C bonds in $\text{Cp}^*_2\text{Ir}_2\text{H}_2(\text{CO})_2$. The predicted Ir–Ir–C bond angles of 84.8° (M06-L) or 86.6° (MPW1PW91) or 87.7° (BP86) are close to the experimental values of 85.1° and 85.4° for $\text{Cp}^*_2\text{Ir}_2\text{H}_2(\text{CO})_2$. The $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structures **Ir-2CO-2S** and **Ir-2CO-3S**, lying 0.3 and $2.1 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-2CO-1S**, are similar to **Ir-2CO-1S** and to each other except for the diverse dihedrals and angles. Thus the C–Ir–Ir–C dihedral angles in **Ir-2CO-1S**, **Ir-2CO-2S**, and **Ir-2CO-3S** are 96.6° , 180° , and 92.3° , respectively.

The next $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure **Ir-2CO-4S**, lying only $4.1 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-2CO-1S**, is a C_{2h} singlet structure with two hydrogen bridges and a terminal CO group on each iridium atom with a *trans* orientation of the two CO groups. Structure **Ir-2CO-8S**, lying $6.9 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-2CO-1S**, is the *cis* isomer corresponding to **Ir-2CO-4S**. Structure **Ir-2CO-5S**, lying $4.7 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-2CO-1S**, has the opposite ligand configuration of **Ir-2CO-8S** with two bridging CO groups and two terminal hydrogen atoms in a *cis* configuration. Structure **Ir-2CO-9S**, lying $8.8 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-2CO-1S**, is the *trans* isomer corresponding to **Ir-2CO-5S**. Structure **Ir-2CO-6S**, lying $6.9 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-2CO-1S**, has one bridging CO group. In **Ir-2CO-6S** two terminal hydrogen atoms are bonded to one of the iridium atoms and one terminal CO group is bonded to the other iridium atom.

Figure 2. Optimized geometries of the nine $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structures including the Ir-Ir distances and relative energies.

Table 1. Comparison of predicted geometrical parameters for the $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure **Ir-2CO-2S** with the experimental values [17] for $\text{Cp}^*\text{Ir}_2\text{H}_2(\text{CO})_2$ determined by X-ray crystallography.

category	experimental	theoretical
Ir-Ir distance	2.730 Å	2.779 Å (M06-L) 2.740 Å (MPW1PW91) 2.769 Å (BP86)
C-Ir(1) distance	1.817 Å	1.834 Å (M06-L)
C-Ir(2) distance	1.829 Å	1.826 Å (MPW1PW91) 1.833 Å (BP86)
Ir-Ir-C(1) angles ^a	85.1°	84.8° (M06-L)
Ir-Ir-C(2) angles ^a	85.4°	86.6° (MPW1PW91) 87.7° (BP86)

^a Ir (1) refers to the upper iridium atom and Ir (2) means the bottom iridium atom in Figure 2.

The final low-energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure **Ir-2CO-7S**, lying $6.4 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-2CO-1S**, is a doubly bridged structure with a bridging CO group and a bridging hydrogen atom. One iridium atom bears a terminal hydrogen atom whereas the other iridium atom bears a terminal CO group with the terminal ligands in a *trans* configuration. The hydrogen bridge is slightly unsymmetrical with Ir–H distances of 1.76 and 1.80 Å. The bridging CO group is considerably more unsymmetrical with Ir–C distances of 1.92 and 2.21 Å, respectively. The Ir–Ir distance in **Ir-2CO-7S** of 2.807 Å (M06-L) corresponds to a formal single bond, thereby giving each iridium atom the favored 18-electron configuration.

3.1.3 $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$. Six singlet $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structures (Figure 3) were optimized. The Ir–Ir distances in these $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structures are predicted to range from ~ 2.50 to 2.62 Å, consistent with Ir=Ir double bonds. The lowest energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structure is a triply bridged C_{2v} structure **Ir-1CO-1S** with one bridging carbonyl group, two bridging hydrogen atoms with Ir–H distances of 1.799 Å, and cyclopentadienyl rings as the only terminal group bonded to each iridium atom. The three bridging groups in **Ir-1CO-1S** combined with the formal Ir=Ir double bond gives each iridium atom the favored 18-electron configuration.

The $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structure **Ir-1CO-2S**, lying only $4.1 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-1CO-1S**, has *trans* stereochemistry with one bridging hydrogen, one terminal hydrogen, and one terminal carbonyl group. The $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structure **Ir-1CO-3S**, lying $7.3 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-1CO-1S**, is the corresponding *cis* isomer. Another stable singlet $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structure **Ir-1CO-4S**, lying $8.3 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-1CO-1S**, has one bridging carbonyl, one bridging hydrogen, and one terminal hydrogen. The formal double bond suggested by the Ir=Ir distances of ~ 2.6 Å in each of these three structures gives each iridium atom the favored 18-electron configuration.

The lowest energy unbridged $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structures **Ir-1CO-5S** and **Ir-1CO-6S**, lying 11.0 and $15.2 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Ir-1CO-1S**, respectively, are a *trans/cis* isomer pair having two terminal hydrogen atoms on one iridium atom and the terminal CO group on the other iridium atom. The less hindered *trans* isomer **Ir-1CO-5S** is the lower energy of these two structures. The Ir=Ir distances of ~ 2.5 Å are ~ 0.1 Å shorter than those in the bridged $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structures. However, they still can be interpreted as the formal double bonds required to give each iridium atom the favored 18-electron configuration.

Figure 3. Optimized geometries of the six $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$ structures including the Ir-Ir distances and relative energies.

3.2 The $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_n$ ($n = 3, 2, 1$) structures

3.2.1 $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$. Ten singlet $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ structures were found within $12 \text{ kcal}\cdot\text{mol}^{-1}$ of the lowest energy structures (Figure 4). All ten structures contain a Os–Os single bond, typically of length $\sim 2.9 \text{ \AA}$. The lowest energy $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ structure **Os-3CO-1S**, as well as the higher energy structures **Os-2CO-2S** and **Os-2CO-6S**, lying 1.9 and $5.4 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Os-3CO-1S**, respectively, are unbridged structures. Two terminal CO groups are bonded to one osmium atom. The third terminal CO group and the two terminal hydrogen atoms are bonded to the other osmium atom. These three $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ structures differ only in the ligand orientations. The two lower energy of these three structures, namely **Os-3CO-1S** and **Os-3CO-2S**, have a *trans* orientation of the Cp rings whereas the higher energy structure **Os-3CO-6S** has a slightly more sterically hindered *cis* orientation of the Cp rings.

The next two $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ structures **Os-3CO-3S** and **Os-3CO-4S** are nearly degenerate in energy, lying 2.4 and $2.7 \text{ kcal}\cdot\text{mol}^{-1}$ above **Os-3CO-1S**. Each structure has a *trans* orientation of the Cp ligands, one bridging CO group, as well as a terminal CO group and a terminal hydrogen bonded to each osmium atom. These structures differ only

in the orientations of the ligands. Considering the Os–Os distances of ~ 2.84 Å as formal single bonds gives each osmium atom the favored 18-electron configuration. The $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ structure **Os-3CO-7S**, lying $6.2 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Os-3CO-1S**, is a closely related structure with a *cis* orientation of the Cp ligands.

Figure 4. Optimized geometries of the ten $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ structures including the Os–Os distances and relative energies.

The $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ structure **Os-3CO-5S**, lying $4.4 \text{ kcal}\cdot\text{mol}^{-1}$ in energy above **Os-3CO-1S**, has two terminal CO groups in a *cis* orientation, one terminal hydrogen

atom, one bridging hydrogen atom, one bridging CO group, and a *cis* orientation of the Cp rings. The predicted Os–Os distance of 2.895 Å (M06-L) is somewhat longer than the lower energy $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ isomers because of the bridging hydrogen atom. It can be interpreted as the formal single bond required to give each osmium atom the favored 18-electron configuration.

The three $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ structures **Os-3CO-7S**, **Os-3CO-8S**, and **Os-3CO-9S**, lying 6.2, 6.5, and 7.9 kcal·mol⁻¹ in energy above **Os-3CO-1S**, respectively, are very similar with one bridging CO group as well as a terminal hydrogen atom and a terminal CO group bonded to each osmium atom. The Cp rings in all three structures have *cis* orientations and the Os–Os distances of ~2.85 Å to ~2.89 Å suggest formal single bonds.

The last singlet $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ structure **Os-3CO-10S**, lying 11.3 kcal/mol in energy above **Os-3CO-1S**, has two bridging CO groups and a *cis* orientation of the Cp rings. One osmium atom is bonded to a terminal CO group. The other osmium atom is bonded to two terminal hydrogen atoms with 1.628 Å Os–H distances.

3.2.2. $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$. Three structures were found for $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ within 10 kcal·mol⁻¹ of the global minimum (Figure 5). The lowest energy $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure **Os-2CO-1S** is a C_{2h} structure with two bridging hydrogen atoms and two terminal CO groups with a *trans* orientation. Structure **Os-2CO-1S** is very close to the experimental $\text{Cp}^*\text{Os}_2\text{H}_2(\text{CO})_2$ structure ($\text{Cp}^* = \eta^5\text{-Me}_5\text{C}_5$), structurally characterized by single-crystal X-ray crystallography (Table 2) [16]. The predicted Os=Os distance in **Os-2CO-1S** of 2.710 Å (M06-L), 2.675 Å (MPW1PW91) or 2.688 Å (BP86) is close to the experimental value of 2.677 Å for $\text{Cp}^*\text{Os}_2\text{H}_2(\text{CO})_2$. The predicted Os–H distances in **Os-2CO-1S** are all the same at 1.817 Å (M06-L), 1.802 Å (MPW1PW91), or 1.814 Å (BP86). The hydrogen atoms were not found in the crystal structure of $\text{Cp}^*\text{Os}_2\text{H}_2(\text{CO})_2$. The predicted Os–Os–C angles of 92.7° (M06-L), 93.8° (MPW1PW91), or 94.4° (BP86) are close to the experimental value of 96.2°. The $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure **Os-2CO-2S**, lying 3.8 kcal·mol⁻¹ in energy above **Os-2CO-1S** is the *cis* isomer corresponding to **Os-2CO-1S**.

The next $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure **Os-2CO-3S**, lying 9.0 kcal·mol⁻¹ in energy above **Os-2CO-1S**, has only a single hydrogen bridge. Thus one osmium atom in **Os-2CO-3S** is bonded to a terminal hydrogen and a terminal CO group whereas the other osmium atom is bonded only to a terminal CO group. The bridging hydrogen atom in **Os-2CO-3S** is slightly unsymmetrical with Os–H distances of 1.797 and 1.832 Å. The Os–Os double bond length of 2.695 Å (M06-L) in **Os-2CO-3S** is predicted to be slightly

shorter than that in **Os-2CO-1S** but likewise can correspond to the formal double bond required to give each of the two osmium atoms the favored 18-electron configuration.

Figure 5. Optimized geometries of the three $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ structures including the Os=Os distances and relative energies.

Table 2. Comparison of the experimental $\text{Cp}^*_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure with the predicted $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure **Os-2CO-1S**.

	Experimental $\text{Cp}^*_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure	Predicted $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure Os-2CO-1S
Os-Os distance	2.677 Å	2.710 Å (M06-L) 2.675 Å (MPW1PW91) 2.688 Å (BP86)
Os-C distance	1.833 Å	1.855 Å (M06-L) 1.849 Å (MPW1PW91) 1.854 Å (BP86)
Os-Os-C angles	96.2°	92.7° (M06-L) 93.8° (MPW1PW91) 94.4° (BP86)

3.2.3 $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})$. Two singlet $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})$ structures were found (Figure 6). The lowest energy structure **Os-1CO-1S** is a triply bridged C_{2v} structure with one bridging CO group and two bridging hydrogen atoms. The equivalent Os-H-Os angles are 86.0°. The Os-C distances to the bridging carbonyl group are 2.048 Å and the Os-H distances to the bridging hydrogen atoms are 1.825 Å. The predicted Os≡Os distance in **Os-1CO-1S** of 2.490 Å (M06-L), 2.455 Å (MPW1PW91), or 2.472 Å (BP86) can correspond to the formal triple bond required to give each osmium atom the favored 18-electron configuration.

Figure 6. Optimized geometries of the two $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})$ structures including the $\text{Os}=\text{Os}$ distances and relative energies.

The $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})$ structure **Os-1CO-1S** appears to be relatively favorable since the next structure in terms of energy, namely **Os-1CO-2S**, lies 36.1 kcal/mol (M06-L) above **Os-1CO-1S**. Structure **Os-1CO-2S** has a bridging CO group and two terminal hydrogen atoms bonded to one of the osmium atoms. The predicted $\text{Os}=\text{Os}$ distance in **Os-1CO-2S** of 2.558 Å (M06-L) is consistent with a formal triple bond. This gives each osmium atom in **Os-1CO-2S** the favored 18-electron configuration if the osmium atom bearing two hydrogen atoms has a formal positive charge balanced by a formal negative charge on the other osmium atom.

3.3 The $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_n$ ($n = 3, 2, 1$) structures

3.3.1 $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$. Five singlet state low-energy $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$ structures were optimized (Figure 7). All of these $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$ structures have $\text{Re}=\text{Re}$ distances ranging from 2.7 to 2.8 Å, which may be interpreted as the formal double bonds required to give each rhenium atom the favored 18-electron configuration. The lowest energy $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$ structure **Re-3CO-1S** has a single hydrogen atom bridging the $\text{Re}=\text{Re}$ double bond of length 2.777 Å (M06-L). One rhenium atom in **Re-3CO-1S** is bonded to the other hydrogen atom and a terminal CO group whereas the other rhenium atom is bonded to the remaining two terminal CO groups. A second $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$ structure **Re-3CO-2S** is essentially degenerate with **Re-3CO-1S** since the predicted energy separation of the two structures is only 0.1 kcal·mol⁻¹ suggesting a fluxional system. Structure **Re-3CO-2S** is geometrically similar to **Re-3CO-1S** except for the bond angles.

Figure 7. Optimized geometries of the five $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$ structures including the Re-Re distances and relative energies.

The next two $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$ structures **Re-3CO-3S** and **Re-3CO-4S**, lying 4.5 and 6.9 $\text{kcal}\cdot\text{mol}^{-1}$ in energy above **Re-3CO-1S**, each have three terminal CO groups and one of the two hydrogen atoms as a bridge between the rhenium atoms. One of the rhenium atoms in these two structures is bonded to two terminal CO groups whereas the other rhenium atom is bonded to one terminal CO group and a terminal hydrogen atom. Interpretation of the Re=Re distances of ~ 2.78 Å in **Re-3CO-3S** and **Re-3CO-4S** as formal double bonds gives each rhenium atom the favored 18-electron configuration.

The next $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$ structure **Re-3CO-5S**, lying 7.7 kcal/mol (M06-L) in energy above **Re-CO-1S**, has a CO group and a hydrogen atom bonded to each Re atom as terminal ligands. The third CO group is a weakly semibridging group with a short Re-C distance of 1.935 Å and a long Re-C distance of 2.635 Å. The Re=Re distance of 2.748 Å (M06-L) is shorter than that in other $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$ structures, possibly because of the semibridging CO group. However, interpreting the Re=Re interaction in **Re-3CO-5S** as a formal double bond gives each rhenium atom the favored 18-electron configuration.

3.3.2 $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_2$. Four singlet state low-energy $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_2$ structures were optimized (Figure 8). All of these structures have a formal $\text{Re}\equiv\text{Re}$ triple bond with

lengths of ~ 2.48 Å thereby giving each rhenium atom the favored 18-electron configuration. The lowest energy of these structures **Re-2CO-1S** is a C_{2v} structure having *cis* stereochemistry with two terminal η^5 -Cp rings, two equivalent terminal hydrogen atoms with Re–H distances of 1.669 Å, and two bridging CO groups with Re–C distances of 2.063 Å and 2.062 Å.

Figure 8. Optimized geometries of the four $Cp_2Re_2H_2(CO)_2$ structures including the Re=Re distances and relative energies.

The second singlet $Cp_2Re_2H_2(CO)_2$ structure **Re-2CO-2S**, lying only $0.6 \text{ kcal}\cdot\text{mol}^{-1}$ (M06-L) in energy above **Re-2CO-1S**, has two different bridging groups, namely one CO group and one hydrogen atom. One rhenium atom in **Re-2CO-2S** is bonded to a terminal hydrogen atom with an Re–H distance of 1.661 Å (M06-L) whereas the other rhenium atom is bonded to a terminal CO group with an Re–C distance of 1.915 Å with *trans* stereochemistry for the terminal Re–H and Re–C bonds. This difference in the terminal ligands on the rhenium atoms in **Re-2CO-2S** leads to asymmetry in the bridging ligands. Thus for the bridging hydrogen atom, the Re–H distances are 1.821 and 1.880 Å whereas for the bridging CO group the Re–C distances are 2.014 and 2.157 Å.

The $Cp_2Re_2H_2(CO)_2$ structure **Re-2CO-4S**, lying 3.9 kcal/mol in energy above **Re-2CO-1S**, is closely related to **Re-2CO-2S** with one bridging CO group and one

bridging hydrogen atom but with *cis* rather than *trans* stereochemistry of the Cp rings. However, the second CO group in **Re-2CO-4S** is a semibridging CO group rather than a terminal CO group. The two Re-C bonds to the bridging CO group in **Re-2CO-4S** are slightly unequal at 2.006 and 2.186 Å. However, the two Re-C bonds differ more significantly at 1.946 and 2.442 Å for the semibridging CO group. The Re=Re distances of ~2.48 Å in **Re-2CO-1S** and **Re-2CO-4S** are in a reasonable range for the formal triple bond required to give each rhenium atom the favored 18-electron configuration.

The $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_2$ structure **Re-2CO-3S**, lying 3.6 kcal·mol⁻¹ in energy above **Re-2CO-1S**, has two semibridging CO groups with short Re-C distances of ~1.95 Å and long Re-C distances of ~2.3 Å. In addition a terminal hydrogen atom is bonded to each rhenium atom in **Re-2CO-3S**. The Re=Re distance of 2.461 Å (M06-L), although significantly shorter than the Re=Re triple bonds in **Re-2CO-1S**, **Re-2CO-2S**, and **Re-2CO-4S**, can correspond to the formal triple bond required to give each rhenium atom the favored 18-electron configuration.

3.3.3 $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$. Four low-energy singlet structures were found for $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ (Figure 9). All four structures have very short Re-Re bond distances of ~2.35 to 2.48 Å, which can be interpreted as the formal quadruple bonds required to give each rhenium atom the favored 18-electron configuration. The four $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structures differ mainly in the nature of the bridging ligands across the formal Re-Re quadruple bond. Thus in the global minimum $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structure **Re-1CO-1S** all three ligands are bridging groups with equal Re-C and Re-H distances, respectively, to each rhenium atom in accord with the C_2 symmetry. However, the $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structures **Re-1CO-2S** and **Re-1CO-3S**, lying 7.4 and 8.0 kcal·mol⁻¹ in energy, respectively, above **Re-1CO-1S**, have a bridging hydrogen atom and a bridging CO group leaving one terminal hydrogen atom. Structures **Re-1CO-2S** and **Re-1CO-3S** are geometrically similar except for the orientation of the Cp rings and the dihedral angles. The $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structure **Re-1CO-4S**, lying 10.3 kcal·mol⁻¹ in energy above **Re-1CO-1S**, has two terminal hydrogen atoms and one semibridging CO group with a short Re-C distances of 1.922 Å and a long Re-C distance of 2.465 Å.

Figure 9. Optimized geometries of the four $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structures including the Re-Re distances and relative energies.

3.4 Thermochemistry.

Table 3 lists the predicted CO dissociation energies for the reactions $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n \rightarrow \text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_{n-1} + \text{CO}$ based on the lowest energy structures using the three different functionals M06-L, BP86, and MPW1PW91. In general the three functionals are in good agreement, typically within 15% or less.

For the iridium system, the CO dissociation energy of $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ to $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2 + \text{CO}$ is rather low at $\sim 10 \text{ kcal}\cdot\text{mol}^{-1}$. However, that of $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ to $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO}) + \text{CO}$ is rather high at $\sim 47 \text{ kcal}\cdot\text{mol}^{-1}$. This is consistent with the isolation of $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ as a stable molecule [17]. The dissociation reactions for the lowest energy $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_n$ structures are all predicted to be highly endothermic. For the osmium system the CO dissociation energies of both $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ and $\text{Cp}_2\text{Os}_3\text{H}_2(\text{CO})_2$ are both relatively high at ~ 34 and $\sim 40 \text{ kcal}\cdot\text{mol}^{-1}$ suggesting that either molecule could be viable. In this case the dicarbonyl $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ is the species that has been synthesized although the tricarbonyl $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ could also be a feasible synthetic objective. None of the $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_n$ ($n = 3, 2, 1$) derivatives are known

experimentally. The rhenium derivative $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_2$ with a formal $\text{Re}=\text{Re}$ triple bond has a very high predicted CO dissociation energy of ~ 70 kcal/mol to give $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ with a formal Re-Re quadruple bond. The CO dissociation energies suggest $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_2$ to be the most promising synthetic target. The experimental CO dissociation energies for the stable metal carbonyls $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Cr}(\text{CO})_6$ of 27, 41, and 37 kcal $\cdot\text{mol}^{-1}$, respectively, [40] can be compared with the predicted CO dissociation energies for the $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($n = 3, 2$) structures in Table 3.

Table 3. CO dissociation energies (kcal $\cdot\text{mol}^{-1}$) for $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir, Os, Re}$; $n = 1, 2, 3$) based on the lowest energy structures by the M06-L, MPW1PW91 and BP86 methods.

Reaction	Functional	CO dissociation energy
$\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3 \rightarrow \text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2 + \text{CO}$	M06-L	11.6
	BP86	11.9
	MPW1PW91	8.7
$\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2 \rightarrow \text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO}) + \text{CO}$	M06-L	46.0
	BP86	48.5
	MPW1PW91	48.9
$\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3 \rightarrow \text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2 + \text{CO}$	M06-L	32.4
	BP86	36.3
	MPW1PW91	32.4
$\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2 \rightarrow \text{Cp}_2\text{Os}_2\text{H}_2(\text{CO}) + \text{CO}$	M06-L	37.2
	BP86	40.9
	MPW1PW91	41.5
$\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3 \rightarrow \text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_2 + \text{CO}$	M06-L	30.9
	BP86	28.2
	MPW1PW91	32.8
$\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_2 \rightarrow \text{Cp}_2\text{Re}_2\text{H}_2(\text{CO}) + \text{CO}$	M06-L	66.4
	BP86	72.2
	MPW1PW91	70.7

3.5 NBO analysis

The analogous lowest energy $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir, Os, Re}$; $n = 3, 2, 1$) structures of are compared in Tables 4 to 6 with respect to the Wiberg bond indices (WBIs), determined by NBO analysis [41] as well as the metal-metal distances, the formal metal-metal bond orders, and the presence of bridging carbonyl groups and/or hydrogen atoms. Previous studies [37] on the WBIs of metal carbonyls show that the WBIs are relatively low compared with the formal bond orders, particularly when the metal-metal bonds are bridged by carbonyl groups.

Table 4. Wiberg bond indices (WBI) of the Ir–Ir bonds, Ir–Ir distances (Å), and the formal Ir–Ir bond orders in the $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_n$ structures ($n = 1, 2, 3$) calculated at the M06-L level of theory.

	Ir-Ir WBI	Ir-Ir Distance (Å)	Bond order	Bridging groups
Ir-1CO-1S	0.49	2.613	2	2H, 1CO
Ir-1CO-2S	0.64	2.620	2	1H
Ir-1CO-3S	0.64	2.623	2	1H
Ir-1CO-4S	0.59	2.621	2	1CO, 1H
Ir-1CO-5S	1.02	2.501	2	None
Ir-1CO-6S	1.02	2.507	2	None
Ir-2CO-1S	0.48	2.770	1	None
Ir-2CO-2S	0.49	2.779	1	None
Ir-2CO-3S	0.49	2.770	1	None
Ir-2CO-4S	0.32	2.855	1	2H
Ir-2CO-5S	0.34	2.708	1	2CO
Ir-2CO-6S	0.41	2.746	1	1CO
Ir-2CO-7S	0.33	2.807	1	1H, 1CO
Ir-2CO-8S	0.32	2.850	1	2H
Ir-2CO-9S	0.33	2.721	1	2CO
Ir-3CO-1S	0.46	2.790	1	None
Ir-3CO-2S	0.09	3.633	0	1CO
Ir-3CO-3S	0.08	3.706	0	1CO
Ir-3CO-4S	0.09	3.662	0	1CO
Ir-3CO-5S	0.08	3.756	0	1CO
Ir-3CO-6S	0.09	3.641	0	1CO
Ir-3CO-7S	0.29	2.829	1	1CO

For the unbridged iridium and osmium structures without the complication of bridging groups, the WBIs for formal double, and single metal-metal bonds in the $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}$, $n = 2, 1$; $\text{M} = \text{Os}$, $n = 3$) structures are ~ 1.0 and ~ 0.5 , respectively (Tables 4 and 5). The WBIs for rhenium-rhenium bonds in the unbridged $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_n$ structures are somewhat lower for a given bond order, i. e. ~ 0.6 for the $\text{Re}=\text{Re}$ double bonds in the unbridged $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$ structures and ~ 1.2 to ~ 1.8 for the $\text{Re}-\text{Re}$ quadruple bonds in the unbridged $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structures. Addition of bridging groups (H and/or CO) across the metal-metal bonds lowers the WBIs significantly for a given bond order. Thus the WBIs for bridged triple, double, and single metal-metal bonds in the $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}$, Os) structures are ~ 0.7 , ~ 0.5 , and ~ 0.4 , respectively. The effect of bridging groups in lowering the effective metal-metal bond order as indicated by a lower WBI value has been attributed to multicenter bonding

involving both metal atoms and the bridging atom(s) [42]. This phenomenon has been examined in greater depth by Ponec using domain averaged Fermi holes [43].

Table 5. Wiberg bond indices (WBI) of the Os-Os bonds, Os-Os distances (Å), and the formal Os-Os bond orders in the $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_n$ structures ($n = 1, 2, 3$) calculated at the M06-L level of theory.

	Os-Os WBI	Os-Os Distance (Å)	Bond order	Bridging groups
Os-1CO-1S	0.77	2.490	3	2H, 1CO
Os-1CO-2S	0.66	2.558	3	1CO
Os-2CO-1S	0.51	2.710	2	2H
Os-2CO-2S	0.50	2.727	2	2H
Os-2CO-3S	0.63	2.695	2	1H
Os-3CO-1S	0.47	2.891	1	None
Os-3CO-2S	0.49	2.887	1	None
Os-3CO-3S	0.41	2.842	1	1CO
Os-3CO-4S	0.40	2.850	1	1CO
Os-3CO-5S	0.48	2.895	1	1CO, 1H
Os-3CO-6S	0.47	2.902	1	None
Os-3CO-7S	0.39	2.874	1	1CO
Os-3CO-8S	0.40	2.856	1	1CO
Os-3CO-9S	0.40	2.882	1	1CO
Os-3CO-10S	0.33	2.810	1	2CO

Table 6. Wiberg bond indices (WBI) of the Re-Re bonds, Re-Re distances (Å), and the formal Re-Re bond orders in the $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_n$ structures ($n = 1, 2, 3$) calculated at the M06-L level of theory.

M06-L(Re-Re)				
	Re-Re WBI	Re-Re Distance (Å)	Bond order	Bridging groups
Re-1CO-1S	1.54	2.451	4	2H, 1CO
Re-1CO-2S	1.48	2.457	4	1H, 1CO
Re-1CO-3S	1.24	2.478	4	1H, 1CO
Re-1CO-4S	1.84	2.357	4	1CO(semi)
Re-2CO-1S	0.97	2.483	3	2CO
Re-2CO-2S	0.95	2.495	3	1CO,1H
Re-2CO-3S	1.07	2.461	3	2CO(semi)
Re-2CO-4S	0.92	2.483	3	1CO, 1H,1CO (semi)
Re-3CO-1S	0.63	2.777	2	1H
Re-3CO-2S	0.58	2.767	2	1H
Re-3CO-3S	0.59	2.791	2	1H
Re-3CO-4S	0.60	2.782	2	1H
Re-3CO-5S	0.69	2.748	2	1CO (semi)

4. Discussion

The two experimentally known $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}; n = 3, 2, 1$) derivatives are both dicarbonyls $\text{Cp}^*_2\text{M}_2\text{H}_2(\text{CO})_2$ ($\text{M} = \text{Ir}$ [17], Os [16]) containing the permethylated Cp^* ligand. Our predicted low-energy structures for the corresponding unsubstituted $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_2$ derivatives agree well with the experimental structures of the corresponding $\text{Cp}^*_2\text{M}_2\text{H}_2(\text{CO})_2$ derivatives. Thus the low energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure **Ir-2CO-2S** (Figure 2), within $0.3 \text{ kcal}\cdot\text{mol}^{-1}$ of the global minimum, has exclusively terminal CO and hydride ligands with an Ir–Ir distance of $\sim 2.8 \text{ \AA}$ suggesting the formal single bond required to give the iridium atom the favored 18-electron configuration. However, the lowest energy $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure **Os-2CO-1S** has the two hydrogen atoms bridging an Os=Os bond of length $\sim 2.71 \text{ \AA}$ as compared with the experimental value of $\sim 2.68 \text{ \AA}$ (Figure 5). Interpretation of this Os=Os interaction as a formal double bond gives each osmium atom the favored 18-electron configuration.

The central $\text{Os}_2(\mu\text{-H})_2$ unit in the $\text{Cp}_2\text{Os}_2(\mu\text{-H})_2(\text{CO})_2$ structure **Os-2CO-1S** may be regarded as a protonated double bond similar to the central $\text{B}_2(\mu\text{-H})_2$ unit in diborane, $\text{B}_2\text{H}_6 = \text{B}_2(\mu\text{-H})_2\text{H}_4$. The experimentally known [44] $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$ has a similar doubly bridged $\text{Re}_2(\mu\text{-H})_2$ unit with an Re=Re distance of $\sim 2.88 \text{ \AA}$. The longer doubly bridged Re=Re distance in $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$ relative to the doubly bridged Os=Os distance in $\text{Cp}_2\text{Os}_2(\mu\text{-H})_2(\text{CO})_2$ can be related to the strong back-bonding of the “extra” CO groups in $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$ relative to the Cp ligands in $\text{Cp}_2\text{Os}_2(\mu\text{-H})_2(\text{CO})_2$. This additional back-bonding can remove more electron density from the central $\text{M}_2(\mu\text{-H})_2$ unit in $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$ relative to $\text{Cp}_2\text{Os}_2(\mu\text{-H})_2(\text{CO})_2$ thereby weakening the metal-metal interaction. Note that the BH_2 , $\text{CpOs}(\text{CO})$, and $\text{Re}(\text{CO})_4$ moieties in $\text{B}_2(\mu\text{-H})_2\text{H}_4$, $\text{Cp}_2\text{Os}_2(\mu\text{-H})_2(\text{CO})_2$, and $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$ are isoelectronic and isolobal.

The potential energy surfaces of some of the $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}; n = 3, 2, 1$) derivatives are rather complicated with isomeric structures having different combinations of bridging CO and H ligands and *trans* and *cis* orientations of the Cp rings having energies within a few $\text{kcal}\cdot\text{mol}^{-1}$. However, the lowest energy structures of the monocarbonyls $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}$) are consistently triply bridged structures with all three ligands bridging the metal-metal bond. The $\text{Cp}_2\text{Os}_2(\mu\text{-H})_2(\mu\text{-CO})$ structure **Os-1CO-1S** of this type is particularly favorable, since it lies $\sim 36 \text{ kcal}\cdot\text{mol}^{-1}$ in energy below the next lowest energy structure **Os-1CO-2S** (Figure 6). In the $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}; n = 3, 2, 1$) structures each hydrogen atom and each CO group are consistently donors of one and two electrons, respectively, regardless of whether they occupy terminal or bridging positions. This means that the complete series of isomeric $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ structures have the same formal M-M bond order.

The 18-electron rule provides reasonable assignments for the formal metal-metal bond orders in the $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}; n = 3, 2, 1$) derivatives. Thus the $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ and $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_3$ systems have formal single metal-metal bonds. These typically have lengths ranging from ~ 2.8 to $2.9 \text{ \AA}$. However, these become shorter approaching $\sim 2.7 \text{ \AA}$ in the structures having bridging CO groups such as the higher energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structures **Ir-2CO-5S**, **Ir-2CO-6S**, and **Ir-2CO-9S**. Similarly, the $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$, $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$, and $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$ systems have formal double metal-metal bonds. These can range in length from ~ 2.5 to $2.6 \text{ \AA}$ for $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})$, $\sim 2.7 \text{ \AA}$ for $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$, and $\sim 2.8 \text{ \AA}$ for $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_3$. There is here a definite increase in the $\text{M}=\text{M}$ double bond length as the number of CO groups is increased. This may be a consequence of the strong back-bonding CO ligands withdrawing electron density from the $\text{M}=\text{M}$ double bond.

The trend continues for the $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ systems with higher formal metal-metal bond orders. None of these systems have yet been realized experimentally. The 18-electron rule predicts formal $\text{M}\equiv\text{M}$ triple bonds for the $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})$ and $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})_2$ structures. Such triple bonds have lengths of $\sim 2.5 \text{ \AA}$ and are bridged by two ligands in the lowest energy structures. At least one of these bridging ligands is a CO group.

The 18-electron rule predicts a formal Re-Re quadruple bond in the $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structures consistent with the relatively short Re-Re distances of $\sim 2.4 \text{ \AA}$ and relatively high WBIs ranging from ~ 1.2 to ~ 1.8 . The lowest energy $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structure **Re-1CO-1S** has all three ligands bridging the Re-Re bond as discussed above. However, the next three higher energy $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structures, lying $\sim 7 \text{ kcal}\cdot\text{mol}^{-1}$ or more in energy above **Re-1CO-1S**, have at least one terminal hydrogen atom.

The 18-electron rule suggests absence of an iridium-iridium bond in the $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structures. Five of the seven lowest-energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structures from **Ir-3CO-2S** to **Ir-3CO-6S**, inclusive, have long non-bonding $\text{Ir}\cdots\text{Ir}$ distances ranging from ~ 3.63 to $\sim 3.76 \text{ \AA}$. However, the lowest-energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structure **Ir-3CO-1S** as well as the higher energy structures **Ir-3CO-7S** have Ir-Ir bonding distances of $\sim 2.8 \text{ \AA}$ consistent with a formal single bond. In **Ir-3CO-1S** the 18-electron configuration is maintained for each iridium atom by migration of a hydrogen atom from rhenium to carbon to give a one-electron donor formyl $-\text{C}(\text{O})\text{H}$ ligand. In **Ir-3CO-7S** the 18-electron configuration is maintained for each iridium atom by slippage of one of the Cp rings to become a trihapto $\eta^3\text{-Cp}$ ligand rather than the usual pentahapto $\eta^5\text{-Cp}$ ligand. However, the tricarbonyl $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ does not appear to be a very favorable system since its CO dissociation energy to give the known $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$ is only $\sim 11 \text{ kcal/mol}$.

5. Conclusions

The $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}; n = 3, 2, 1$) systems, including the experimentally known and structurally characterized permethylated derivatives $\text{Cp}^*_2\text{M}_2\text{H}_2(\text{CO})_2$ ($\text{Cp}^* = \eta^5\text{-Me}_5\text{C}_5$; $\text{M} = \text{Ir}$ [17], Os [16]), provide examples of binuclear structures having metal-metal bonds of formal orders ranging from zero to four consistent with the 18-electron rule. The low-energy $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_3$ structures lacking a direct iridium-iridium bond necessarily have a bridging CO group holding together the two iridium atoms. For $\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$, low-energy unbridged structures are found corresponding to the experimental unbridged $\text{Cp}^*_2\text{Ir}_2\text{H}_2(\text{CO})_2$ structure. However, for $\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$ the lowest energy structure has two hydrogen atoms bridging the formal $\text{Os}=\text{Os}$ double bond similar to the experimental doubly bridged $\text{Cp}^*_2\text{Os}_2\text{H}_2(\text{CO})_2$ structure. The central $\text{Os}_2(\mu\text{-H})_2$ protonated double bond is similar to the central $\text{B}_2(\mu\text{-H})_2$ protonated double bond in diborane. The lowest energy structures of the monocarbonyls $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})$ have all three ligands ($2\text{H} + \text{CO}$) bridging a central metal-metal bond. The $\text{Cp}_2\text{Re}_2\text{H}_2(\text{CO})$ structures provide examples of both bridged and unbridged structures containing formal Re-Re quadruple bonds with highly bridged structures being preferred energetically.

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Supporting Information. Tables S1 to S9: Total energies (E , in hartree), relative energies (ΔE , in kcal/mol), numbers of imaginary vibrational frequencies (N_{imag}), and Ir-Ir distances ($\text{\AA}$) for the optimized $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}; n = 1, 2, 3$) structures; Tables S10 to S12: Wiberg bond indices (WBIs) of bonds, bond distances, and the bond order analysis in the structures of $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}; n = 1, 2, 3$) calculated at the MPW1PW91 level of theory; Tables S13 to S64: Coordinates of the optimized $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}; n = 1, 2, 3$) structures; Tables S65 to S73: Harmonic vibrational frequencies of the optimized $\text{Cp}_2\text{M}_2\text{H}_2(\text{CO})_n$ ($\text{M} = \text{Ir}, \text{Os}, \text{Re}; n = 1, 2, 3$) structures; Complete Gaussian Reference.

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$\text{Cp}_2\text{Ir}_2\text{H}_2(\text{CO})_2$

$\text{Cp}_2\text{Os}_2\text{H}_2(\text{CO})_2$