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Unsaturated Binuclear Cyclopentadienylosmium Carbonyl Derivatives: Comparison with Their Iron Analogues

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

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

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The binuclear cyclopentadienylosmium carbonyls $Cp_2Os_2(CO)_n$ ($Cp = \eta^5\text{-}C_5H_5$; $n = 4, 3, 2$) have been studied by density functional theory (DFT). The unbridged $Cp_2Os_2(CO)_4$ structure found experimentally is predicted to be of lower energy than the doubly bridged structures *cis*- and *trans*-$Cp_2Os_2(CO)_2(\mu\text{-}CO)_2$, in contrast to the analogous iron system. However, the energy differences are rather small (~5 kcal/mol). The $Cp_2Os_2(CO)_3$ system differs from its iron analogue in that the triplet structure $Cp_2Os_2(\mu\text{-}CO)_3$ analogous to the known, stable $Cp_2Fe_2(\mu\text{-}CO)_3$ lies at least ~12 kcal/mol above the lowest energy singlet structure. Thus the three lowest lying $Cp_2Os_2(CO)_3$ structures are all singlet structures, which are either unbridged or doubly bridged. The iron and osmium dicarbonyl systems $Cp_2M_2(CO)_2$ (M = Fe, Ru) are analogous in that the lowest energy structures are doubly bridged with short M≡M distances suggesting the formal triple bonds required to give both metal atoms the favored 18-electron configuration. The product observed in 2001 by Bitterwolf, Linehan, and Shade in the photolysis of $Cp_2Os_2(CO)_4$ in a Nujol matrix at 90 K appears to be singlet $Cp_2Os_2(\mu\text{-}CO)_2$ rather than the originally suggested triplet $Cp_2Os_2(\mu\text{-}CO)_3$.

1. Introduction

The very stable binuclear cyclopentadienylmetal carbonyls $Cp_2M_2(CO)_4$ (Figure 1: M = Fe, Ru, Os; $Cp = \eta^5\text{-}C_5H_5$) are important molecules in the organometallic chemistry of the group 8 metals. For the readily available iron and ruthenium compounds the structures with two bridging carbonyl groups are known to be preferred over the unbridged structures. For $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ both the *trans*[1−3] and *cis*[4] doubly bridged isomers have been characterized structurally by X-ray diffraction.

The analogous osmium compound $Cp_2Os_2(CO)_4$ has proven to be significantly more difficult to synthesize[5−7] and thus has been less studied than its iron and ruthenium analogues. Of particular interest is the observation that the unbridged structure is preferred over the doubly bridged structures for $Cp_2Os_2(CO)_4$ in contrast to the iron and ruthenium analogues.[8] However, for the pentamethylcyclopentadienyl derivative $(\eta^5\text{-}Me_5C_5)_2Os_2(CO)_4$ the *trans* doubly bridged structure is preferred over the unbridged structure, as shown not only by its ν(CO) frequencies but also by a structure determination using X-ray diffraction.[7]

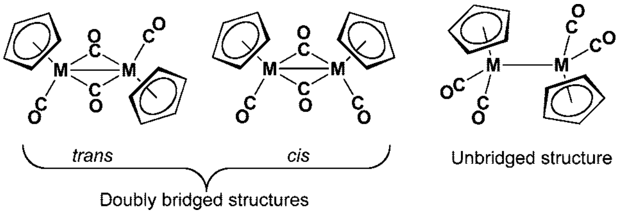

Figure 1. Structures found for $Cp_2M_2(CO)_4$ derivatives (M = Fe, Ru, Os).

Some unsaturated $Cp_2Fe_2(CO)_n$ derivatives are known as isolable compounds ($n = 3$) or probable reaction intermediates ($n = 2$). Thus the tricarbonyl $Cp_2Fe_2(\mu\text{-}CO)_3$ with a formal Fe=Fe double bond has been synthesized by the photolysis of $Cp_2Fe_2(CO)_4$.[9−11] The corresponding permethylated derivative, namely, $(\eta^5\text{-}Me_5C_5)_2Fe_2(\mu\text{-}CO)_3$, has been isolated in the pure state and shown by X-ray diffraction to have three bridging CO groups and an iron−iron distance consistent with the double bond required to give both iron atoms the favored 18-electron configuration.[12] However, $Cp_2Fe_2(\mu\text{-}CO)_3$ is found to exhibit paramagnetism consistent with a triplet electronic state, suggesting that its Fe=Fe double bond is analogous to the double bond in dioxygen. The dicarbonyl $Cp_2Fe_2(CO)_2$ is predicted by DFT to have two bridging carbonyl groups and an Fe≡Fe

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* Corresponding authors. E-mail: qsli@bit.edu.cn; rbking@chem.uga.edu.

[†] Beijing Institute of Technology.

[‡] South China Normal University.

[§] University of Georgia.

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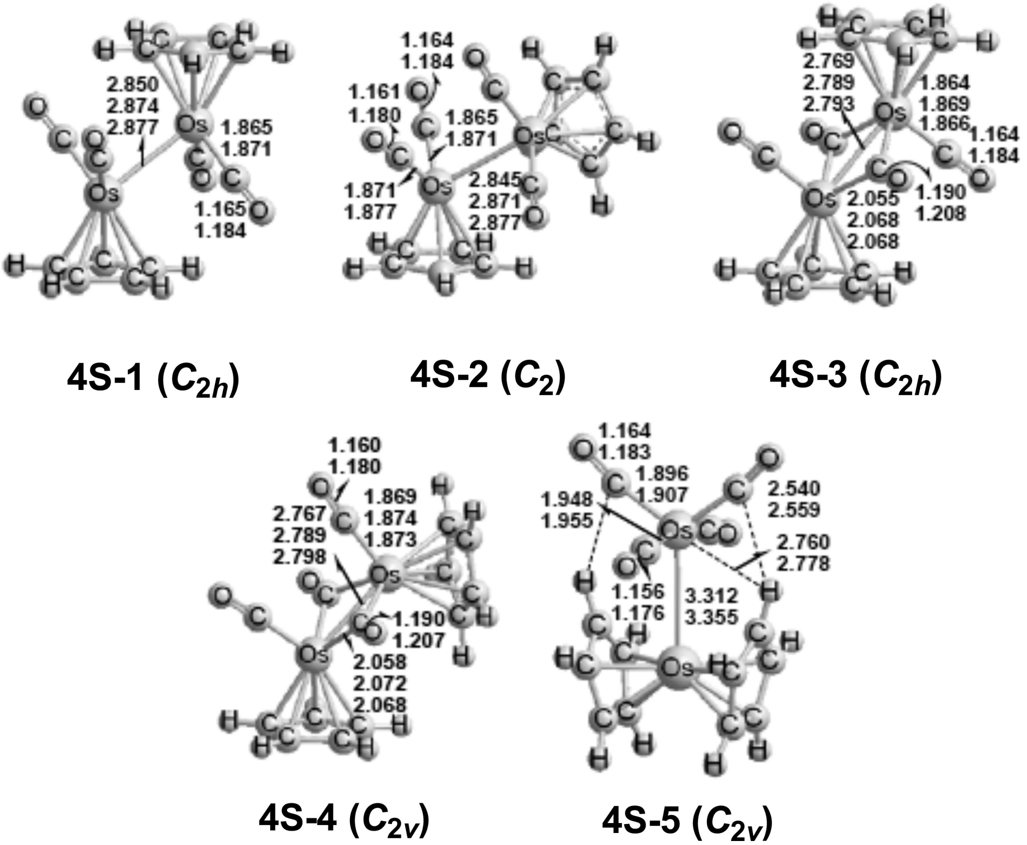

4S-1 (C_{2h}) **4S-2** (C_2) **4S-3** (C_{2h})

4S-4 (C_{2v}) **4S-5** (C_{2v})

Figure 2. Structures for $Cp_2Os_2(CO)_4$. The bond distances are in Å. The values on the top are obtained by the MPW1PW91 method, those on the second line by the BP86 method. The third line data are from ref 7 by the B3LYP method.

Table 1. Total Energy (*E*, in hartree), Relative Energy (Δ*E*, in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimag), and Os−Os Bond Distances (Å) for the $Cp_2Os_2(CO)_4$ Structures

		4S-1 (C_{2h})	**4S-2** (C_2)	**4S-3** (C_{2h})	**4S-4** (C_{2v})	**4S-5** (C_{2v})
MPW1PW91	*E*	−1022.01564	−1022.01111	−1022.01088	−1022.00867	−1021.94706
	Δ*E*	0	2.8	3.0	4.4	43.0
	Nimag	0	0	0	1(21*i*)	1(18*i*,3*i*)
	Os−Os	2.850	2.845	2.769	2.767	3.312
BP86	E	−1022.43102	−1022.42629	−1022.43089	−1022.42756	−1022.36554
	Δ*E*	0	3.0	0.1	2.2	41.1
	Nimag	0	0	2(16*i*,12*i*)	1(23*i*)	1(7*i*)
	Os−Os	2.874	2.871	2.789	2.789	3.355

distance consistent with the triple bond required to give both iron atoms the favored 18-electron configuration.[13] Some evidence has been presented for the existence of an unbridged isomer of $Cp_2Fe_2(CO)_2$ as a photolysis product of $Cp_2Fe_2(CO)_4$ in low-temperature matrices.[14] A similar unsaturated species, $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2$, is a likely intermediate in the preparation of the very stable tetramer $(\eta^5\text{-}C_5H_5)_4Fe_4(\mu\text{-}CO)_4$ by the pyrolysis of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)_2$ in a solvent such as toluene.[15]

The reported chemistry of unsaturated $Cp_2Os_2(CO)_n$ derivatives is much more limited, as expected because of the high cost of osmium. Bitterwolf, Linehan, and Shade[16] reported the photolysis of $Cp_2Os_2(CO)_4$ in a Nujol matrix at 90 K to give an unsaturated $Cp_2Os_2(CO)_n$ derivative, assumed to be $Cp_2Os_2(\mu\text{-}CO)_3$, analogous to the known[11,12] $Cp_2Fe_2(\mu\text{-}CO)_3$ on the basis of the observation of a new ν(CO) frequency at 1802 cm^{-1}.

This paper presents a density functional theory study of the cyclopentadienylosmium carbonyl derivatives $Cp_2Os_2(CO)_n$ ($n = 4, 3, 2$) with the following two specific objectives:

(1) Comparison of the favored structures of $Cp_2Os_2(CO)_n$ derivatives with the corresponding $Cp_2Fe_2(CO)_n$ derivatives. This point is particularly interesting in view of the known preference of $Cp_2Fe_2(CO)_4$ for doubly bridged structures but that of $Cp_2Os_2(CO)_4$ for unbridged structures.

(2) Identification of the product observed by Bitterwolf, Linehan, and Shade[16] in their 2001 matrix photolysis experiments.

2. Theoretical Methods

Electron correlation effects were considered by employing density functional theory (DFT), which has evolved as a practical and effective computational tool, especially for organometallic

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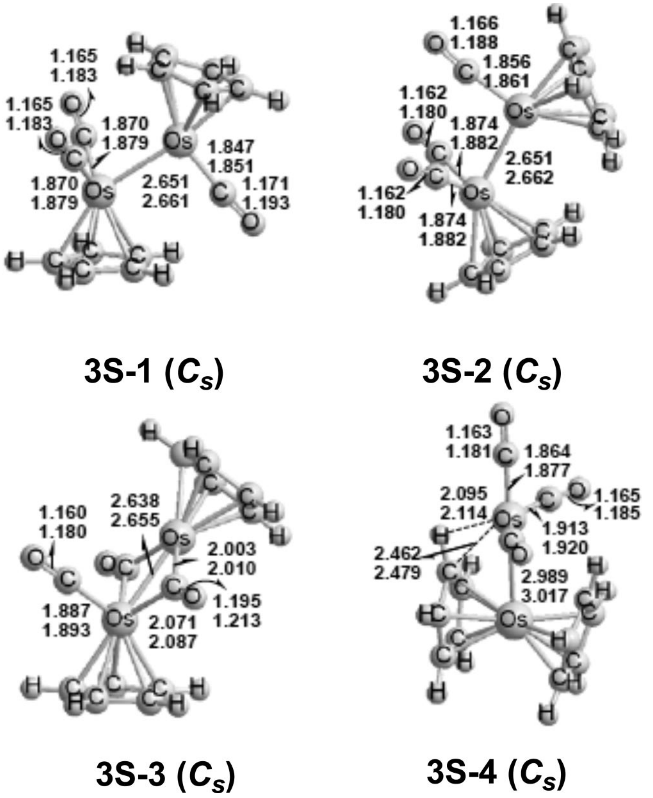

3S-1 (C_s) **3S-2 (C_s)**

3S-3 (C_s) **3S-4 (C_s)**

Figure 3. Four low-lying singlet structures for $Cp_2Os_2(CO)_3$. In Figures 3−6 the bond distances are given in Å, with the upper values obtained by the MPW1PW91 method and the lower values by the BP86 method.

compounds.[17−25] Two DFT methods, namely, BP86 and MPW1PW91, were used in this work. The BP86 method is a pure DFT method combining Becke's 1988 exchange functional with Perdew's 1986 correlation functional.[26,27] The MPW1PW91 method[28] is a so-called second-generation[29] functional, namely, a combination of the modified Perdew−Wang exchange functional with the Perdew−Wang 91 gradient-correlation functional.[30] The MPW1PW91 method has been found to be more suitable for geometry optimization of the second- and third-row transition metal systems, while the BP86 method usually provides better vibrational frequencies.[31,32]

For the third-row transition metals, the large numbers of electrons can increase exponentially the computational efforts. In order to reduce the cost, the SDD (Stuttgart−Dresden ECP plus DZ),[33] effective core potential (ECP) basis set, which includes relativistic effects, was employed for the osmium atoms in this study. For the C and O atoms, the double-ζ plus polarization (DZP) basis sets were used. They are the Huzinaga−Dunning contracted double-ζ contraction sets[34,35] plus a set of spherical harmonic d polarization functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$ and designated as (9s5p1d/4s2p1d). For H, a set of p polarization functions, $\alpha_p(H) = 0.75$, was added to the Huzinaga−Dunning DZ set. These computational methods for osmium carbonyl derivatives have been tested previously for homoleptic trinuclear[36] and tetranuclear[37] osmium carbonyl derivatives where comparison with experimental data for the known $Os_3(CO)_{12}$, $Os_4(CO)_{16}$, $Os_4(CO)_{15}$, and $Os_4(CO)_{14}$ can be used to evaluate alternative DFT methods.

The geometries of all structures were fully optimized using the two selected DFT methods along with the SDD ECP basis sets. Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates at the same levels. The corresponding infrared intensities were also evaluated analytically. All of the computations were carried out with the Gaussian 03 program.[38] The fine grid (75, 302) was the default for evaluating integrals numerically. The finer grid (120, 974) was used for more precise resolution of the imaginary vibrational frequencies. The tight (10^{-8} hartree) designation was the default for the self-consistent-field (SCF) convergence. All of the predicted triplet structures were found to have negligible spin contamination, with $\langle S^2 \rangle$ values very close to the ideal value of $S(S+1) = 2$.

A total of 21 structures were predicted for $Cp_2Os_2(CO)_n$ ($n = 4$, 3, 2). Structures within 30 kcal/mol of the global minima are considered in detail in the text. A summary of the vibrational frequencies and geometries of all structures are given in the Supporting Information.

3. Results

3.1. $Cp_2Os_2(CO)_4$. Two pairs of *trans* and *cis* structures of $Cp_2Os_2(CO)_4$ are predicted having almost degenerate energies within 5.0 kcal/mol, thereby suggesting a highly fluxional system (Figure 2 and Table 1). The global minimum is found to be an unbridged *trans* structure, **4S-1**, with C_{2h} symmetry. An unbridged *cis* structure, **4S-2**, with C_2 symmetry is predicted lying ~3.0 kcal/mol (Table 1) above the global minimum **4S-1**. Both structures are predicted to be genuine minima, having all real vibrational frequencies. The Os−Os bond distances in the two structures are predicted to fall in the range 2.845−2.874 Å (Figure 2), suggesting a normal Os−Os single bond, thereby giving all osmium atoms the favored 18-electron configurations. Our theoretical Os−Os bond distance agrees well with the Os−Os distance of 2.877 Å predicted in a previously reported DFT study using the B3LYP method.[7]

The doubly bridged structures **4S-3** and **4S-4** (Figure 2 and Table 1) are the second pair of *trans* and *cis* structures for $Cp_2Os_2(CO)_4$. The *trans* structure **4S-3** (C_{2h}) is predicted to lie 3.0 kcal/mol (MPW1PW91) or 0.1 kcal/mol (BP86) above the global minimum **4S-1**, while the relative energy for the *cis* structure **4S-4** (C_{2v}) is 4.4 kcal/mol (MPW1PW91) or 2.2 kcal/mol (BP86) above **4S-1**. However, the previous B3LYP study[7]

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Table 2. Total Energy (*E*, in hartree), Relative Energy (Δ*E*, in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimag), and Os−Os Bond Distances (Å) for the Singlet Structures of $Cp_2Os_2(CO)_3$

		3S-1 (C_s)	**3S-2** (C_s)	**3S-3** (C_s)	**3S-4** (C_s)
MPW1PW91	*E*	−908.62945	−908.62156	−908.62050	−908.60910
	Δ*E*	0.0	5.0	5.6	12.8
	Nimag	0	0	1(13*i*)	0
	Os−Os	2.650	2.651	2.638	2.989
BP86	*E*	−909.01148	−909.00327	−909.00748	−908.99004
	Δ*E*	0.0	5.2	2.5	13.5
	Nimag	0	0	0	0
	Os−Os	2.657	2.662	2.655	3.017

Table 3. Total Energy (*E*, in Hartree), Energy Relative to the Singlet 3S-1 (Δ*E*, in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimag), Re−Re Bond Distances (Å), and Spin Contamination $\langle S^2\rangle$ for Each of the Triplet $Cp_2Os_2(CO)_3$ Structures

		3T-1 (C_s)	**3T-2** (C_s)	**3T-3** (C_s)
MPW1PW91	*E*	−908.60087	−908.60014	−908.59241
	Δ*E*	17.9	18.4	23.2
	Nimag	2(27*i*,24*i*)	0	0
	Re−Re	2.551	2.721	2.726
	$\langle S^2\rangle$	2.02	2.02	2.02
BP86	*E*	−908.99222	−908.97616	−908.96844
	Δ*E*	12.1	22.2	27.0
	Nimag	2(26*i*,23*i*)	1(12*i*)	0
	Re−Re	2.575	2.728	2.731
	$\langle S^2\rangle$	2.00	2.02	2.01

predicted a significantly higher relative energy for these two doubly bridged structures, i.e., 11.5 and 12.6 kcal/mol, respectively, for **4S-3** and **4S-4**. Structure **4S-3** for $Cp_2Os_2(CO)_4$ is predicted to have two small imaginary vibrational frequencies at 16*i* cm^{-1} and 12*i* cm^{-1} (BP86). These frequencies most likely arise from numerical integration errors, since they are removed by using a finer integration grid (120, 974). Structure **4S-4** is also found to have a small imaginary vibrational frequency at 23*i* (BP86), which decreases to 11*i* cm^{-1} (BP86) when the finer integration grid (120, 974) is used.

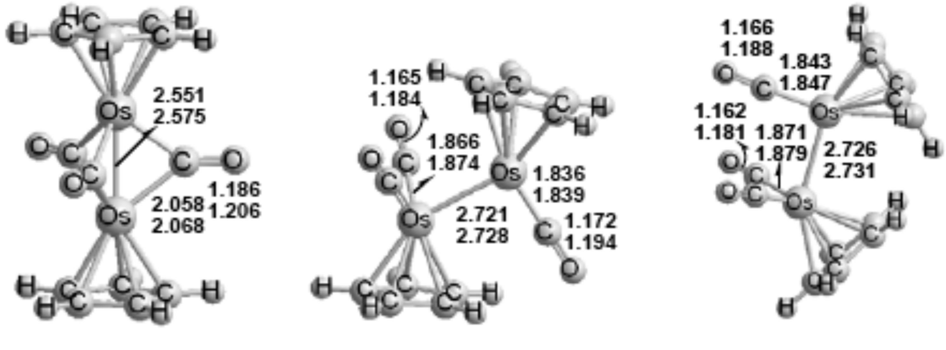
The predicted Os−Os bond distances in the doubly bridged structures **4S-3** and **4S-4** are ~0.1 Å shorter than those in the unbridged structures **4S-1** and **4S-2**. This bond shortening is a typical consequence of the two bridging carbonyl groups. Our theoretical Os−Os bond distance of 2.769 Å (MPW1PW91) or 2.789 Å (BP86) for **4S-3** agrees well with the experimental X-ray Os−Os bond distance[7] of 2.7668(7) Å for (η^5-$Me_5C_5)_2Os_2(CO)_2(\mu$-$CO)_2$, which is found to have a structure analogous to **4S-3** but with complete substitution of the Cp hydrogens with methyl groups.

Another type of $Cp_2Os_2(CO)_4$ structure, namely, Cp_2-Os−Os$(CO)_4$ (**4S-5** in Figure 2), has both Cp rings bonded to one osmium atom and the four carbonyl groups bonded to the other osmium atom. Structure **4S-5** is predicted to lie at a much higher energy than the other $Cp_2Os_2(CO)_4$ structures, namely, 43.0 kcal/mol (MPW1PW91) or 41.1 kcal/mol (BP86) above the global minimum **4S-1**. Structure **4S-5** is predicted to have a negligible imaginary vibrational frequency at 7*i* (BP86), which is removed by using a finer integration grid (120, 974). The Os−Os bond distance in **4S-5** is predicted to be 3.312 Å (MPW1PW91) or 3.355 Å (BP86). Structure **4S-5** can be derived from $Os(CO)_5$ by replacement of one of its carbonyl groups by an osmocene ligand with one of the osmium lone pairs of the osmocene acting as a base. The basic properties of osmocene have been previously observed in its protonation by trifluoroacetic acid to give the Cp_2OsH^+ cation.[39,40]

3.2. $Cp_2Os_2(CO)_3$. Four low-lying singlet structures (Figure 3 and Table 2) are predicted for $Cp_2Os_2(CO)_3$. The global minimum **3S-1** is a C_s unbridged *trans* structure, with an Os=Os bond length in **3S-1** predicted to be ~0.2 Å shorter than that of **4S-1** (Figure 2). This is in accord with the dipolar $\mathrm{Os}\underline{\rightarrow}\mathrm{Os}$ double bond required to give both osmium atoms 18-electron configurations. Structure **3S-1** (C_s) can be derived from **4S-1** (C_{2h}) by removal of one carbonyl group, thereby reducing the symmetry from C_{2h} to C_s with concurrent shortening of the Os=Os distance from that of a single bond to that of a dipolar double bond.

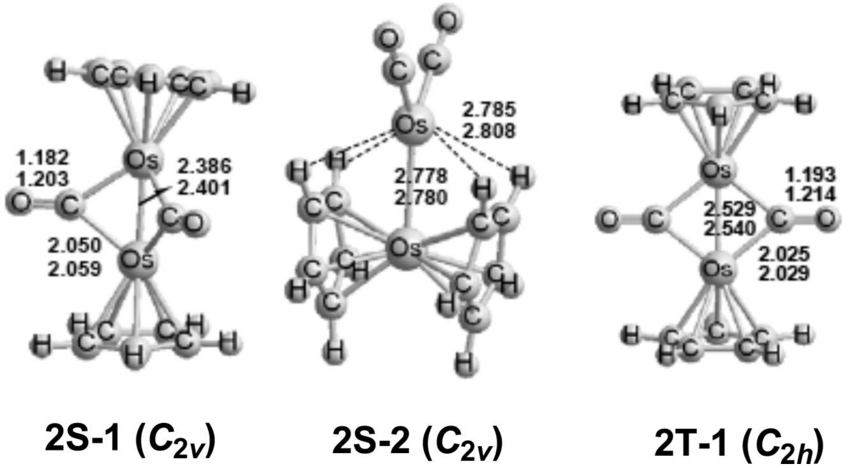
An unbridged *cis* structure, **3S-2** (Figure 3 and Table 2), is predicted to lie above **3S-1** by ~5 kcal/mol. The $\mathrm{Os}\underline{\rightarrow}\mathrm{Os}$ dipolar double bond length in **3S-2** is predicted to be almost the same as that in **3S-1** and likewise corresponds to the dipolar double bond required to give each of the two osmium atoms an 18-electron configuration. Structure **3S-2**, like **3S-1**, can also be derived from corresponding *cis* structure **4S-2** (C_2) by removal of one carbonyl.

A doubly bridged C_s structure, **3S-3**, for $Cp_2Os_2(CO)_3$ (Figure 3 and Table 2) is derived from **4S-3** or **4S-4** (Figure 2) by removal of one terminal carbonyl group. Structure **3S-3** is predicted to lie 5.6 kcal/mol (MPW1PW91) or 2.5 kcal/mol (BP86) above the global minimum **3S-1**, with all real vibrational frequencies. The predicted Os=Os bond distance of 2.638 Å (MPW1PW91) or 2.655 Å (BP86) falls in the range of the



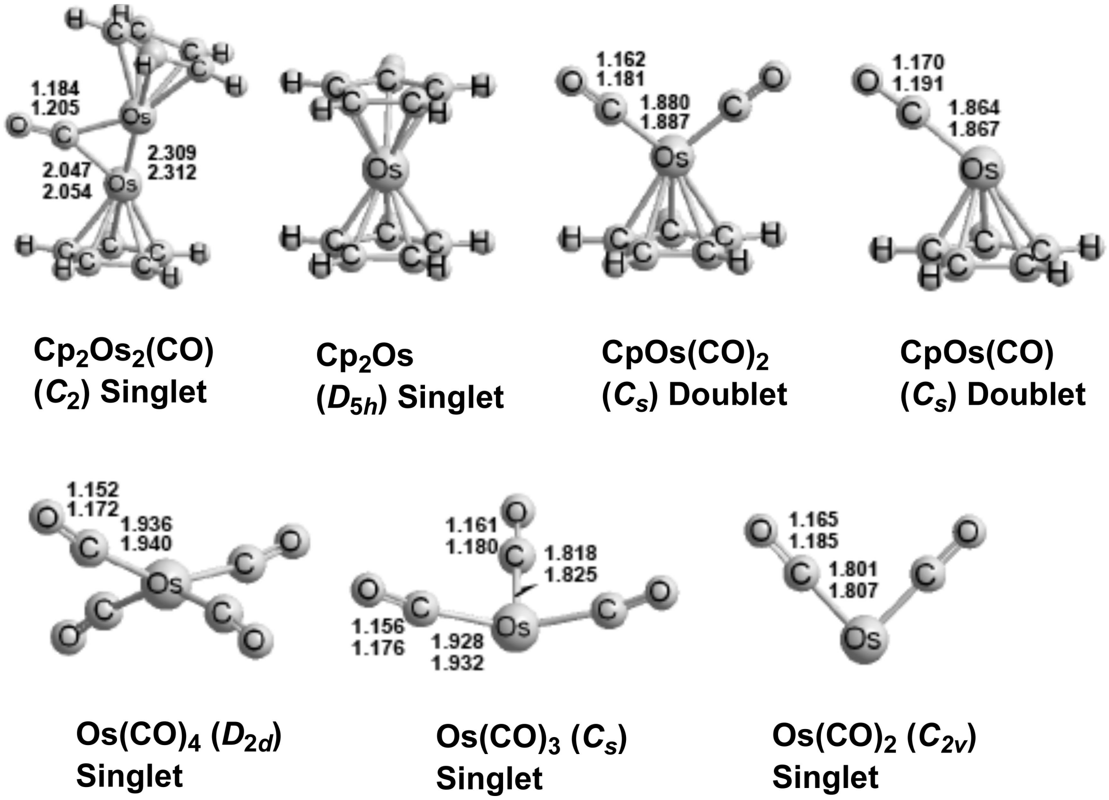
3T-1 (C_s) **3T-2 (C_s)** **3T-3 (C_s)**

Figure 4. Three triplet structures for $Cp_2Os_2(CO)_3$.



2S-1 (C_{2v}) **2S-2** (C_{2v}) **2T-1** (C_{2h})

Figure 5. Optimized structures for $Cp_2Os_2(CO)_2$.



$Cp_2Os_2(CO)$ (C_2) Singlet

Cp_2Os (D_{5h}) Singlet

$CpOs(CO)_2$ (C_s) Doublet

$CpOs(CO)$ (C_s) Doublet

$Os(CO)_4$ (D_{2d}) Singlet

$Os(CO)_3$ (C_s) Singlet

$Os(CO)_2$ (C_{2v}) Singlet

Figure 6. Optimized structures for $Cp_2Os_2(CO)$, Cp_2Os, $CpOs(CO)_n$, and $Os(CO)_n$ fragments.

Table 4. Total Energy (*E*, in hartree), Relative Energy (Δ*E*, in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimag), Os−Os Bond Distances (Å), and Spin Contamination ⟨*S*²⟩ for the $Cp_2Os_2(CO)_2$ Structures

		2S-1 (C_{2v})	**2S-2** (C_{2v})	**2T-1** (C_{2h})
MPW1PW91	*E*	−795.25755	−795.23826	−795.23457
	Δ*E*	0	12.1	14.4
	Nimag	0	0	0
	Os−Os	2.386	2.778	2.529
	$\langle S^2\rangle$	0	0	2.04
BP86	*E*	−795.61488	−795.58219	−795.58973
	Δ*E*	0	20.5	15.8
	Nimag	0	0	1(12*i*)
	Os−Os	2.401	2.780	2.540
	$\langle S^2\rangle$	0	0	2.01

double bond required to give both osmium atoms 18-electron configurations, similar to **3S-1** and **3S-2**.

The rather different $Cp_2Os-Os(CO)_3$ structure **3S-4** (Figure 3), with one osmium atom bearing both Cp rings and the other osmium atom bearing only terminal carbonyl groups, is predicted to have all real vibrational frequencies and lies 12.8 kcal/mol (MPW1PW91) or 13.5 kcal/mol (BP86) above the global minimum **3S-1**. The Os−Os bond distance in **3S-4** is ~0.3 Å shorter than that in **4S-5**. The predicted Os−H distance of 2.095 Å (MPW1PW91) or 2.114 Å (BP86) between the "top" hydrogen atom of the left Cp ring and the "top" osmium atom in Figure 3 is very short, suggesting an agostic hydrogen forming a C−H−Os three-center, two-electron bond.

A C_s triply bridged structure, **3T-1** (Figure 4 and Table 3), is predicted to be the lowest lying triplet structure of $Cp_2Os_2(CO)_3$. However, it lies 17.9 kcal/mol (MPW1PW91) or 12.1 kcal/mol (BP86) above the global minimum **3S-1**. Structure **3T-1** is predicted to have two small imaginary

Table 5. Total Energy (E, in hartree), Number of Imaginary Vibrational Frequencies (Nimag), and Spin Contamination $\langle S^2 \rangle$ for $Cp_2Os_2(CO)$, Cp_2Os_2 and $CpOs(CO)_n$

		$Cp_2Os_2(CO)$	Cp_2Os	$CpOs(CO)_2$	$CpOs(CO)$
MPW1PW91	*E*	−681.83939	−477.82339	−510.96534	−397.55215
	Nimag	0	0	0	0
	$\langle S^2 \rangle$	0	0	0.75	0.78
BP86	*E*	−682.16882	−477.98454	−511.17346	−397.72496
	Nimag	0	0	0	0
	$\langle S^2 \rangle$	0	0	0.75	0.76

Table 6. Total Energy (*E*, in hartree) for $Os(CO)_n$

		$Os(CO)_4$	$Os(CO)_3$	$Os(CO)_2$
MPW1PW91	*E*	−544.11479	−430.73469	−317.35731
BP86	*E*	−544.37246	−430.95514	−317.54002

Table 7. Bond Dissociation Energies (kcal/mol) for the Successive Removal of Carbonyl Groups from the $Cp_2Os_2(CO)_n$ Derivatives and for the Dissociation of the Binuclear Cyclopentadienylosmium Carbonyls into Mononuclear Fragments

	MPW1PW91	BP86
$Cp_2Os_2(CO)_4$ (**4S-1**) → $Cp_2Os_2(CO)_3$ (**3S-1**) + CO	54.6	54.9
$Cp_2Os_2(CO)_4$ (**4S-1**) → $2CpOs(CO)_2$	53.3	52.8
$Cp_2Os_2(CO)_3$ (**3S-1**) → $Cp_2Os_2(CO)_2$ (**2S-1**) + CO	45.6	40.3
$Cp_2Os_2(CO)_3$ (**3S-1**) → $CpOs(CO)_2$ + $CpOs(CO)$	70.2	70.9
$Cp_2Os_2(CO)_2$ (**2S-1**) → $Cp_2Os_2(CO)$ + CO	74.6	71.4
$Cp_2Os_2(CO)_2$ (**2S-1**) → $2CpOs(CO)$	96.2	103.5

Table 8. Disproportionation Energies (kcal/mol)

	MPW1PW91	BP86
$2Cp_2Os_2(CO)_3$ (**3S-1**) → $Cp_2Os_2(CO)_4$ (**4S-1**) + $Cp_2Os_2(CO)_2$ (**2S-1**)	−9.0	−14.5
$2Cp_2Os_2(CO)_2$ (**2S-1**) → $Cp_2Os_2(CO)_3$ (**3S-1**) + $Cp_2Os_2(CO)$	29.0	31.1

Table 9. Energies (kcal/mol) for the Dissociation of $Cp_2Os{-}Os(CO)_n$ into $Cp_2Os + Os(CO)_n$

	MPW1PW91	BP86
$Cp_2Os{-}Os(CO)_4$ (**4S-5**) → $Cp_2Os + Os(CO)_4$	48.6	46.4
$Cp_2Os{-}Os(CO)_3$ (**3S-4**) → $Cp_2Os + Os(CO)_3$	44.8	45.0
$Cp_2Os{-}Os(CO)_2$ (**2S-2**) → $Cp_2Os + Os(CO)_2$	48.2	56.7

vibrational frequencies at 26*i* and 23*i* cm^{-1} (BP86), which collapse to a single negligible 2*i* cm^{-1} frequency by using a finer grid (120, 974). Thus structure **3T-1** can be regarded as a true minimum. The Os=Os bond distance of 2.551 Å (MPW1PW91) or 2.575 Å (BP86) in **3T-1** is the shortest found in any of the predicted structures of $Cp_2Os_2(CO)_3$. The Os=Os double bond in **3T-1** consists of one two-electron σ bond and two orthogonal one-electron π bonds and is thus analogous to the double bond in dioxygen with two unpaired electrons. The analogous $Cp_2Fe_2(\mu\text{-}CO)_3$ structure is known experimentally as a compound sufficiently stable for structure determination by X-ray diffraction.[11,12]

A pair of *trans* and *cis* unbridged triplet structures **3T-2** and **3T-3** (Figure 4), geometrically similar to the singlet **3S-1** and **3S-2**, is predicted to lie ~20 kcal/mol higher in energy than the analogous singlet structures (Table 3). Structure **3T-2** is predicted to have a small imaginary vibrational frequency at 12*i* cm^{-1} (BP86), which is removed using the finer integration grid (120, 974). Structure **3T-3** is a genuine minimum, having all real vibrational frequencies. The Os−Os bond lengths of these two structures are predicted to fall in the narrow range 2.721−2.731 Å, which is roughly 0.07 Å longer than the analogous singlet structures. These bond lengths are consistent with the Os→Os dative single bonds required to give both osmium atoms the 17-electron configurations for a triplet spin state.

3.3. $Cp_2Os_2(CO)_2$. Three energetically low-lying structures are found for $Cp_2Os_2(CO)_2$ (Figure 5 and Table 4). The global minimum for $Cp_2Os_2(CO)_2$ is a C_{2v} doubly bridged singlet structure **2S-1**, having all real vibrational frequencies (Table 4). Structure **2S-1** may be derived from **3S-3** (Figure 3) by removing the single terminal CO group, leaving only the two bridging carbonyl groups. The Os−Os distance is concurrently shortened from 2.638 Å (MPW1PW91) or 2.655 Å (BP86) to 2.386 Å (MPW1PW91) or 2.401 Å (BP86), consistent with the Os$\equiv$Os triple bond required by the 18-electron rule.

A C_{2v} singlet $Cp_2Os{-}Os(CO)_2$ structure (**2S-2** in Figure 5 and Table 4) with all real vibrational frequencies is predicted to lie ~12 kcal/mol (MPW1PW91) or ~20 kcal/mol (BP86) above the global minimum **2S-1**. Structure **2S-2** has one osmium atom with only Cp rings and the other osmium atom with only carbonyl groups. Structure **2S-2** can be derived from **4S-5** by removal of two CO groups from the $Os(CO)_4$ segment. The Os−Os bond distance in **2S-2** is predicted to be ~0.2 Å shorter than that in **3S-4**, suggesting an increased formal bond order consistent with the greater degree of unsaturation.

A triplet doubly bridged C_{2h} structure for $Cp_2Os_2(CO)_2$ is predicted to lie 14.4 kcal/mol (MPW1PW91) or 15.8 kcal/mol (BP86) above the global minimum **2S-1**. Structure **2T-1** is predicted to have a small imaginary vibrational frequency at 12*i* cm^{-1} (BP86), which is removed by using a finer grid (120, 974). The Os=Os bond distance in **2T-1** is predicted to be ~0.15 Å longer than the presumed Os$\equiv$Os triple bond in **2S-1**. This is consistent with the double bond required to give both osmium atoms in **2T-1** the 17-electron arrangements consistent with the triplet spin state.

3.4. $Cp_2Os_2(CO)$, Cp_2Os, $CpOs(CO)_n$, and $Os(CO)_n$ Fragments. In order to determine the dissociation energies of $Cp_2Os_2(CO)_n$ derivatives into two mononuclear $CpOs(CO)_m$ fragments or into $Cp_2Os + Os(CO)_n$ fragments, the mononuclear $CpOs(CO)_m$ and $Os(CO)_n$ derivatives were also investigated using the same DFT methods. The optimized structures and total energies of $Cp_2Os_2(CO)$, Cp_2Os, $CpOs(CO)_m$ (m = 2, 1), and $Os(CO)_n$ (n = 4, 3, 2) are shown in Figure 6 as well as Tables 5 and 6.

3.5. Dissociation and Disproportionation Reactions. The bond dissociation energies (BDE) for loss of one carbonyl group from $Cp_2Os_2(CO)_n$ to give $Cp_2Os_2(CO)_{n-1}$ and the dissociation of $Cp_2Os_2(CO)_n$ into mononuclear fragments are shown in Table 7. These dissociation energies for the lowest energy $Cp_2Os_2(CO)_n$ structures are all seen to be highly endothermic. The lowest of these dissociation energies is 45.6 kcal/mol (MPW1PW91) or 40.3 kcal/mol (BP86) for the carbonyl dissociation of $Cp_2Os_2(CO)_3$. All of the other dissociation energies are predicted to be more than 50 kcal/mol.

Table 8 lists the energies for the disproportionation reactions $2Cp_2Os_2(CO)_n \rightarrow Cp_2Os_2(CO)_{n+1} + Cp_2Os_2(CO)_{n-1}$. These data indicate that $Cp_2Os_2(CO)_3$ is thermodynamically unstable with respect to such disproportionation. However, $Cp_2Os_2(CO)_2$ is thermodynamically stable with respect to disproportionation.

The dissociation energies of the derivatives of the type $Cp_2Os{-}Os(CO)_n$ into $Cp_2Os + Os(CO)_n$ fragments are listed

Table 10. Infrared ν(CO) Stretching Frequencies (cm^{-1}) Predicted for $Cp_2Os_2(CO)_n$ (infrared intensities in parentheses are in km/mol, bridging ν(CO) frequencies are in bold, experimental data are in *italics*)

	MPW1PW91	BP86	B3LYP[7]
4S-1 (C_{2h})	2030 (b_g, 0), 2040 (a_u, 1844), 2074 (b_u, 1335), 2097 (a_g, 0)	1920 (b_g, 0), 1929 (a_u, 1549), 1962 (b_u, 1071), 1981 (a_g, 0)	1938 (1597), 1967 (1121)
exptl	*1915, 1960*;[6] 1932, 1969, 2015(w)[7]; *1927, 1971*;[8] *1931, 1967, 2010(w)*[16]		
4S-2 (C_2)	2044 (b, 1188), 2046 (a, 276), 2075 (b, 591), 2122 (a, 1257)	1932 (b, 993), 1935 (a, 245), 1965 (b, 481), 2003 (a, 1006)	1941 (1039), 1943 (258), 1968 (526), 2010 (1061)
4S-3 (C_{2h})	1862 (a_u, 1215), 1894 (a_u, 0), 2058 (b_u, 1794), 2077 (a_u, 0)	1765 (a_u, 983), 1789 (a_u, 0), 1941 (b_u, 1536), 1960 (a_u, 0)	1776 (991), 1953 (1566)
4S-4 (C_{2v})	1863 (b_1, 1222), 1896 (a_1, 8), 2068 (b_2, 310), 2113 (a_1, 1617)	1766 (b_1, 989), 1791 (a_1, 8), 1951 (b_2, 335), 1992 (a_1, 1319)	1776 (1000), 1805(9), 1960 (301), 2000 (1398)
4S-5 (C_{2v})	2035 (b_2, 1284), 2049 (a_1, 935), 2066 (b_1, 1558), 2150 (a_1, 251)	1922 (b_2, 1035), 1934 (a_1, 744), 1940 (b_1, 1295), 2020 (a_1, 253)	
3S-1 (C_s)	2017 (a′, 1174), 2034 (a″, 931), 2086 (a′, 531)	1898 (a′, 912), 1927 (a″, 788), 1976 (a′, 474)	
3S-2 (C_s)	2034 (a′, 572), 2054 (a″, 956), 2110 (a′, 1264)	1916 (a′, 555), 1946 (a″, 808), 1996 (a′, 957)	
3S-3 (C_s)	1840 (a″, 1252), 1873 (a′, 23), 2091 (a′, 963)	1740 (a″, 1015), 1767 (a′, 17), 1969 (a′, 827)	
3S-4 (C_s)	2011 (a″, 1694), 2038 (a′, 715), 2116 (a′, 781)	1895 (a″, 1332), 1924 (a′, 509), 1995 (a′, 732)	
3T-1 (C_s)	1893 (a″, 1097), 1893 (a′, 1101), 1941 (a′, 0)	1780 (a″, 860), 1780 (a′, 864), 1824 (a′, 0)	
3T-2 (C_s)	2014 (a′, 1142), 2031 (a″, 964), 2083 (a′, 485)	1896 (a′, 875), 1924 (a″, 812), 1970 (a′, 443)	
3T-3 (C_s)	2037 (a′, 445), 2051 (a″, 1000), 2109 (a′, 1341)	1919 (a′, 464), 1942 (a″, 828), 1992 (a′, 1022)	
2S-1 (C_{2v})	1919 (b_1, 1312), 1939 (a_1, 320)	1803 (b_1, 996), 1823 (a_1, 257)	
2S-2 (C_{2v})	1988 (b_2, 1241), 2058 (a_1, 1117)	1884 (b_2, 1006), 1947 (a_1, 896)	
2T-1 (C_{2h})	1848 (a_u, 1168), 1862 (a_g, 0)	1731 (a_u, 890), 1738 (a_g, 0)	
$CpOs(CO)_2$	2052 (a″, 1230), 2111 (a′, 961)	1935 (a″, 1004), 1989 (a′, 762)	1955, 2008[41]
exptl	*1938, 2003*[41]		
CpOs(CO)	2031 (a′, 1258)	1909 (a′, 969)	

in Table 9. These processes are seen to be unfavorable, owing to the required energies ranging from 44.8 to 56.7 kcal/mol.

3.6. Carbonyl Stretching Frequencies. The predicted ν(CO) vibrational frequencies (cm^{-1}) and their infrared intensities for cyclopentadienylosmium carbonyl derivatives $Cp_2Os_2(CO)_n$ ($n = 4, 3, 2$) are reported in Table 10. Usually the ν(CO) frequencies predicted by the MPW1PW91 functional are found more than 100 cm^{-1} higher than the BP86 values, and the latter are close to the experimental results.

The infrared ν(CO) vibrational frequencies (cm^{-1}) for $CpOs(CO)_2$ and CpOs(CO) predicted by DFT are also listed in Table 10. The predicted ν(CO) vibrational frequencies of doublet $CpOs(CO)_2^{\bullet}$ at 1935 and 1989 cm^{-1} by the BP86 method are close to the experimental ν(CO) frequencies[41] of 1938 and 2003, which were assigned in 2005 to $CpOs(CO)_2^{\bullet}$ generated by the laser flash photolysis of $Cp_2Os_2(CO)_4$.

4. Discussion

4.1 Comparison of Analogous $Cp_2Os_2(CO)_n$ and $Cp_2Fe_2(CO)_n$ Derivatives. 4.1.1. $Cp_2Os_2(CO)_4$ versus $Cp_2Fe_2(CO)_4$. The osmium and iron systems are very different since the unbridged structure $Cp_2Os_2(CO)_4$ is the lowest energy structure for the osmium derivative, but the *trans* and *cis* isomers of the doubly bridged structure $Cp_2Fe_2(CO)_2(\mu\text{-}CO)_2$ are the lowest energy structures for the iron derivative (Figure 1). However, for $Cp_2Os_2(CO)_4$ the predicted energy difference between the favored unbridged structure and the doubly bridged structure is less than 5 kcal/mol (Table 1). This is consistent with the experimental observation that for the corresponding pentamethylcyclopentadienylosmium derivative the doubly bridged structure $(\eta^5\text{-}Me_5C_5)_2Os_2(CO)_2(\mu\text{-}CO)_2$ rather than the unbridged structure is the one found experimentally.[7] Thus the complete substitution of methyl groups for hydrogen atoms in $Cp_2Os_2(CO)_4$ is enough to change the favored structure from an unbridged to a doubly bridged structure.

4.1.2. $Cp_2Os_2(CO)_3$ versus $Cp_2Fe_2(CO)_3$. Here the difference between the analogous osmium and iron systems is the most significant. For osmium the three lowest energy structures with energies within 6 kcal/mol (Table 2) are singlet structures with the global minimum being an unbridged structure (**3S-1** in Figure 3). The lowest lying triplet structure is the triply bridged $Cp_2Os_2(\mu\text{-}CO)_3$ at 17.9 kcal/mol (MPW1PW91) or 12.1 kcal/mol (BP86) above the global minimum. However, for the corresponding iron system the analogous triplet triply bridged $Cp_2Fe_2(\mu\text{-}CO)_3$ not only is predicted by DFT to be the lowest energy structure but also is stable enough to be isolated under ambient conditions and structurally characterized by X-ray diffraction.[11,12]

4.1.3. $Cp_2Os_2(CO)_2$ versus $Cp_2Fe_2(CO)_2$. Here the two metals are very similar. Thus the lowest energy predicted structures are the C_{2v} doubly bridged structures $Cp_2M_2(\mu\text{-}CO)_2$ with a relatively short M≡M distance, suggesting the formal triple bond needed to give both metals the favored 18-electron configuration.

4.2. Interpretation of Experimental Data. The only experimental work on unsaturated $Cp_2Os_2(CO)_n$ is reported in the

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(40) Shubina, E. S.; Krylov, A. N.; Kreindlin, A. Z.; Rybinskaya, M. I.; Epstein, L. M. *J. Organomet. Chem.* **1994**, *465*, 259.

(41) Zhang, J.; Grills, D. C.; Huang, K. W.; Fujita, E.; Bullock, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 15684.

2001 paper by Bitterwolf, Linehan, and Shade (BLS).[16] These authors describe the photolysis of $Cp_2Os_2(CO)_4$ in frozen Nujol at 90 K to give a product exhibiting a bridging ν(CO) frequency at 1802 cm^{-1} but no terminal ν(CO) frequencies. They make the very reasonable assumption that the osmium system is like the iron system so that their photoproduct is therefore the triplet $Cp_2Os_2(\mu\text{-}CO)_3$, analogous to the known[11,12] $Cp_2Fe_2(\mu\text{-}CO)_3$. Their assignment of the triply bridged tricarbonyl structure $Cp_2Os_2(\mu\text{-}CO)_3$ corresponding to our **3T-1** (Figure 4) for this product is consistent with our predicted ν(CO) frequency of 1780 cm^{-1} (BP86) for **3T-1** (Table 10).

Despite the good agreement between our predicted and the experimental ν(CO) frequency of the BLS photoproduct for the formulation $Cp_2Os_2(\mu\text{-}CO)_3$ (**3T-1**), our detailed DFT studies on the $Cp_2Os_2(CO)_3$ structures (Figures 3 and 4 and Tables 2 and 3) cause us to question this interpretation of the BLS experimental data. The triplet structure $Cp_2Os_2(\mu\text{-}CO)_3$ (**3T-1** in Figure 4 and Table 3) has a predicted energy at least 12 kcal/mol above the lowest energy singlet $Cp_2Os_2(CO)_3$ structure. Furthermore, conversion of singlet $Cp_2Os_2(CO)_4$ to triplet $Cp_2Os_2(\mu\text{-}CO)_3$ requires a change in the spin state and therefore an intersystem crossing in terms of the photochemistry. These difficulties with the formulation of the BLS photoproduct as $Cp_2Os_2(\mu\text{-}CO)_3$ led us to investigate other possible interpretations of the BLS experimental data.

In the search for possible alternative interpretations of the BLS data, we note that the lowest energy structure for the dicarbonyl is $Cp_2Os_2(\mu\text{-}CO)_2$ (**2S-1** in Figure 5) with two bridging carbonyl groups and no terminal carbonyl groups. The strongest predicted ν(CO) frequency for **2S-1** by BP86 is 1803 cm^{-1} (Table 10), which is remarkably close to the 1802 cm^{-1} ν(CO) reported by BLS.[16] The second ν(CO) frequency for **2S-1** at 1823 cm^{-1} (Table 10) is predicted to have about one-fourth the relative intensity of the 1803 cm^{-1} frequency and might well correspond to the "hump" at ~1820 cm^{-1} in the bottom spectrum in Figure 3 of the BLS paper.[16] This "hump" at ~1820 cm^{-1} was sufficiently close to the noise level that it was understandably ignored by BLS.

The energetics of the disproportionation reactions $2Cp_2Os_2(CO)_n \rightarrow Cp_2Os_2(CO)_{n+1} + Cp_2Os_2(CO)_{n-1}$ ($n = 3, 2$) also support formulation of the BLS photoproduct as a $Cp_2Os_2(CO)_2$ derivative rather than a $Cp_2Os_2(CO)_3$ derivative (Table 8). Thus $Cp_2Os_2(CO)_3$ is theremodynamically unstable with respect to disproportionation into $Cp_2Os_2(CO)_4$ + $Cp_2Os_2(CO)_2$, whereas $Cp_2Os_2(CO)_2$ is thermodynamically stable with respect to an analogous disproportionation into $Cp_2Os_2(CO)_3$ + $Cp_2Os_2(CO)$. For this reason there is a good chance that $Cp_2Os_2(CO)_3$, if formed, would disproportionate into $Cp_2Os_2(CO)_2$ + $Cp_2Os_2(CO)_4$ so that a dicarbonyl, rather than a tricarbonyl, would then be the observed final product.

In summary, the ν(CO) frequency data of the $Cp_2Os_2(CO)_n$ derivatives predicted by our DFT studies (Table 10) are not sufficient to distinguish between triplet $Cp_2Os_2(\mu\text{-}CO)_3$ (**3T-1** in Figure 4) and singlet $Cp_2Os_2(\mu\text{-}CO)_2$ (**2S-1** in Figure 5) as possible photoproducts in an experimental reaction mixture. However, the fact that singlet $Cp_2Os_2(\mu\text{-}CO)_2$ (**2S-1**) is the lowest energy $Cp_2Os_2(CO)_2$ structure whereas triplet $Cp_2Os_2(\mu\text{-}CO)_3$ (**3T-1**) is a higher energy $Cp_2Os_2(CO)_3$ structure leads us to suggest that BLS observed the singlet dicarbonyl $Cp_2Os_2(\mu\text{-}CO)_2$ (**2S-1**) rather than the triplet tricarbonyl $Cp_2Os_2(\mu\text{-}CO)_3$ (**3T-1**) in their Nujol matrix photolysis studies of $Cp_2Os_2(CO)_4$.[16] This suggestion is also consistent with the energetics of $Cp_2Os_2(CO)_n$ disproportionation reactions as noted above.

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Supporting Information Available: Tables S1−S7: Theoretical harmonic vibrational frequencies for $Cp_2Os_2(CO)_4$ (6 structures), $Cp_2Os_2(CO)_3$ (10 structures), and $Cp_2Os_2(CO)_2$ (7 structures) using the BP86 method; Tables S8−S31: Theoretical Cartesian coordinates for $Cp_2Os_2(CO)_4$ (6 structures), $Cp_2Os_2(CO)_3$ (10 structures), and $Cp_2Os_2(CO)_2$ (7 structures) using the MPW1PW91 method; complete Gaussian 03 reference (ref 38). This material is available free of charge via the Internet at http://pubs.acs.org.

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