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Efficient Synthesis of the Os−Os Dimers $[Cp(CO)_2Os]_2$, $[Cp^*(CO)_2Os]_2$, and $[(^iPr_4C_5H)(CO)_2Os]_2$ and Computational Studies on the Relative Stabilities of Their Geometrical Isomers

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The Os−Os dimer $[Cp(CO)_2Os]_2$ was synthesized in good yield by reaction of $Cp(CO)_2OsI$ with NaK. The related Cp* dimer $[Cp^*(CO)_2Os]_2$ ($Cp^* = \eta^5$-C_5Me_5) was prepared by reaction of $Cp^*(CO)_2OsH$ with 2,2′-azobis(isobutyrylnitrile) (AIBN). In contrast to $[Cp(CO)_2Os]_2$, which has only terminal CO ligands, spectroscopic and crystallographic data indicate that $[Cp^*(CO)_2Os]_2$ has two bridging CO ligands. Reaction of tetraisopropylcyclopentadiene with $[(CO)_3OsI]_2$ provides $(^iPr_4C_5H)(CO)_2OsI$, which can be converted to $(^iPr_4C_5H)(CO)_2OsH$ through reduction with NaK followed by treatment with EtOH. Reaction of $(^iPr_4C_5H)(CO)_2OsH$ with AIBN gives $[(^iPr_4C_5H)(CO)_2Os]_2$, which is much more soluble than $[Cp^*(CO)_2Os]_2$. DFT (B3LYP) calculations on these Os−Os dimers reveal the energetics of different geometrical isomers. The anti and gauche isomers of $[Cp(CO)_2Os]_2$, with terminal CO ligands, are significantly more stable than the trans and cis isomers with bridging CO ligands, while the stability of the anti isomer of $[Cp^*(CO)_2Os]_2$ is similar to that of its trans isomer. Computations on the energetics of the isomers with a $[C_5(CF_3)_5]$ ligand suggest that the difference observed for Cp and Cp* complexes is mainly due to electronic rather than steric effects of the Cp groups.

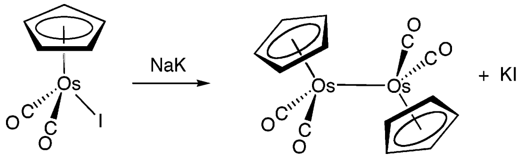
Introduction

The Fe−Fe-bonded dimer $[Cp(CO)_2Fe]_2$ is one of the most thoroughly studied organometallic dimers.[1] It is readily prepared on a large scale and is commercially available and inexpensive. The analogous Ru complex $[Cp(CO)_2Ru]_2$ is also well-known.[2] In contrast, far fewer studies have been carried out on the Os analogue $[Cp(CO)_2Os]_2$ and the Cp* analogue ($Cp^* = \eta^5$-C_5Me_5) $[Cp^*(CO)_2Os]_2$ has received very little attention. We have begun to study photochemical reactions of $[Cp(CO)_2Os]_2$ and related complexes and have found carbon-to-metal hydrogen atom transfer from hydrocarbons to the Os radical $Cp(CO)_2Os^\bullet$.[3] We report new synthetic methods for the preparation of $[Cp(CO)_2Os]_2$ and $[Cp^*(CO)_2Os]_2$ that provide these dimers in higher yields than in previous reports. We have also prepared an analogue with a bulky substituted Cp ligand, $[(^iPr_4C_5H)(CO)_2Os]_2$. New synthetic procedures are also reported for the osmium hydride complexes $Cp(CO)_2OsH$ and $Cp^*(CO)_2OsH$. Computational studies have been carried out to evaluate the relative stabilities of the geometrical isomers of the dimers $[Cp(CO)_2Os]_2$ and $[Cp^*(CO)_2Os]_2$.

Results and Discussion

Synthesis of $[Cp(CO)_2Os]_2$. The Os−Os-bonded dimer $[Cp(CO)_2Os]_2$ was first reported in 1962 by Fischer and Bittler,[4] but it was obtained in only 1.8% yield. A 40% yield of $[Cp(CO)_2Os]_2$ was reported from the reaction of $[(CO)_3OsCl_2]_2$ and $Na^+C_5H_5^-$ in 1967.[5] Herrmann and co-workers reported[6] a 58% yield of $[Cp(CO)_2Os]_2$ from the reaction of $Cp(CO)_2OsH$ with $Ph_3C^+PF_6^-$ followed by NEt_3.

The osmium iodide complex $Cp(CO)_2OsI$ is readily and reproducibly prepared from $Os_3(CO)_{12}$ by a previously reported procedure[7] and is a convenient, air-stable precursor to $[Cp(CO)_2Os]_2$. We have found that the reaction of $Cp(CO)_2OsI$ with NaK in THF at room temperature provides an excellent route to $[Cp(CO)_2Os]_2$, which was isolated in 77−94% yield (eq 1).



(1)

A plausible mechanism involves reduction of $Cp(CO)_2OsI$ to the osmium anion $[Cp(CO)_2Os]^-$, which could displace iodide from the remaining starting material $Cp(CO)_2OsI$, leading to $[Cp(CO)_2Os]_2$. Many metal dimers are reduced to metal anions

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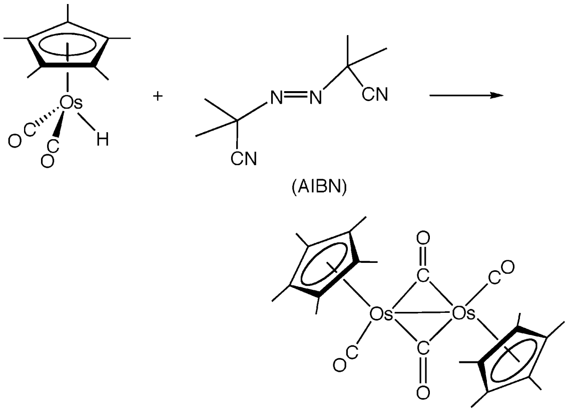
using NaK,[8] including the Fe complex $[Cp(CO)_2Fe]_2$. Under our conditions, further reaction of $[Cp(CO)_2Os]_2$ to the osmium anion $[Cp(CO)_2Os]^-$ was not observed as a significant byproduct when the reaction is stopped after all the $Cp(CO)_2OsI$ is consumed. At longer reaction times, however, NaK reacts with the dimer $[Cp(CO)_2Os]_2$ to form $[Cp(CO)_2Os]^-K^+$, which has IR bands at 1889 and 1808 cm^{-1} in THF. These bands are at slightly lower energy than those we recently found for $[Cp(CO)_2Os]^-Li^+(DME)$, which has IR absorptions at 1901 and 1823 cm^{-1} in THF.[3] The differences in the spectra are likely due to the changes in the cation (K^+ vs Li^+), particularly owing to differences in ion pairing, which have been analyzed[9] for $[Cp^*(CO)_2Os]^-Li^+$ and were reviewed for other metal carbonyl anions.[10]

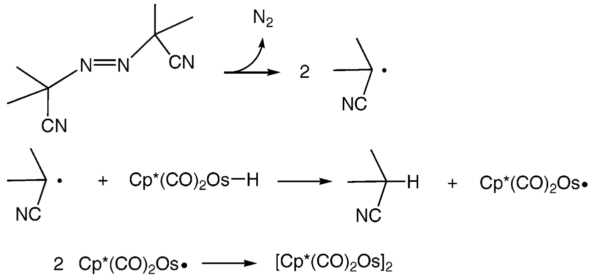
Synthesis of $[Cp^*(CO)_2Os]_2$. An analogous complex with Cp* ligands, $[Cp^*(CO)_2Os]_2$, has been studied even less than $[Cp(CO)_2Os]_2$. Weber and Bungardt reported the isolation of $[Cp^*(CO)_2Os]_2$ in 3.7% yield from the reaction of $Os_3(CO)_{12}$ and C_5Me_5H in refluxing decalin. The attempted preparation of $[Cp^*(CO)_2Os]_2$ (by analogy to eq 1) from the reaction of $Cp^*(CO)_2OsI$ with NaK resulted in the formation of $Cp^*(CO)_2Os^-K^+$, which give two broad IR bands at 1870 and 1775 cm^{-1} in THF, as the main product together with a low yield of $[Cp^*(CO)_2Os]_2$, which was detected by IR spectroscopy. We believe that the same mechanism is involved as in the case of the reaction of $Cp(CO)_2OsI$ with NaK but that displacement of iodide from $Cp^*(CO)_2OsI$ by $Cp^*(CO)_2Os^-$ is slow, presumably for steric reasons, so that reduction to the osmium anion is the predominant reaction under these conditions.

When $Cp^*(CO)_2OsH$ is heated with excess 2,2′-azobis(isobutyrylnitrile) (AIBN) in hexane at 80 °C, the dimer $[Cp^*(CO)_2Os]_2$ precipitates from the reaction mixture and can be readily isolated in 50% yield (eq 2). Similar yields were obtained when the synthesis was carried out in benzene (47% yield) or THF (46% yield).



(2)

Scheme 1



The proposed mechanism is shown in Scheme 1. Thermolysis of AIBN produces the radical $(CH_3)_2(CN)C^\bullet$, which is proposed to abstract a hydrogen atom from $Cp^*(CO)_2OsH$, producing the osmium-centered radical $Cp^*(CO)_2Os^\bullet$. Hydrogen atom transfers from metal hydrides to carbon-centered radicals are well-documented.[11] Such reactions are typically endothermic, since M−H bonds are normally much weaker than C−H bonds. We found that the Os−H bond of $Cp(CO)_2Os{-}H$ is unusually strong for a transition-metal−hydride bond; our experimental measurements set a lower limit of 82 kcal/mol for the Os−H bond (80.1 kcal/mol calculated).[3] We computed (DFT; B3LYP) that the bond dissociation energy of the C−H bond of $(CH_3)_2(CN)C{-}H$ is 84 kcal/mol. Thus, the metal-to-carbon hydrogen atom transfer in the second step of Scheme 1 is roughly thermoneutral. The computed barrier for this hydrogen atom transfer is 15.7 kcal/mol. Dimerization of the osmium radical $Cp^*(CO)_2Os^\bullet$ is irreversible under these conditions and generates the Os−Os-bonded dimer $[Cp^*(CO)_2Os]_2$.

Norton and co-workers found that trityl radical substituted with *tert*-butyl groups on the para position of the Ph ring can be used to abstract hydrogen atoms from metal hydrides, and they reported the kinetics of the metal-to-carbon hydrogen atom transfer reactions.[12] The metal radicals formed in this reaction dimerize, forming M−M dimers. Surprisingly, the reaction of Gomberg's dimer[13] (the dimer of $Ph_3C^\bullet$) with $Cp^*(CO)_2OsH$ or $Cp(CO)_2OsH$ did not produce the expected Os−Os dimers; a reaction did occur, but the products have not been identified.

The dimer $[Cp^*(CO)_2Os]_2$ is nearly insoluble in hexane and has low solubility in THF or CH_2Cl_2. In contrast, $[Cp(CO)_2Os]_2$ is soluble in hexane. This is opposite of the expected trend, where substitution of Cp by Cp* often increases the solubility of organometallic complexes. One reason for this difference is that $[Cp(CO)_2Os]_2$ and $[Cp^*(CO)_2Os]_2$ have different structures. The IR spectrum of $[Cp^*(CO)_2Os]_2$ in CH_2Cl_2 exhibits a band at 1708 cm^{-1} assigned to a bridging CO ligand, along with a band for terminal CO ligands at 1909 cm^{-1}. In contrast, $[Cp(CO)_2Os]_2$ has only terminal CO ligands.

The product-forming step in the synthesis of $[Cp^*(CO)_2Os]_2$, dimerization of metal-centered radicals to generate a metal−metal-bonded complex, is well-precedented for many metal carbonyl systems.[14] A major intermediate produced upon photolysis of $[Cp(CO)_2Fe]_2$[15] is the iron-centered radical $Cp(CO)_2Fe^\bullet$, which dimerizes with a second-order rate constant of $k = 3 \times 10^9\ M^{-1}\ s^{-1}$ at 20 °C.[16] In contrast, $Cp(CO)_2Os^\bullet$ does not cleanly dimerize but rather undergoes reactions that appear to involve a C−H bond on the Cp ring.[3,17]

Structure of $[Cp^*(CO)_2Os]_2$. The structure of $[Cp^*(CO)_2Os]_2$ was determined by single-crystal X-ray diffraction. Details of the crystallographic data are given in Table 1, and selected bond distances are provided in Table 2. An ORTEP drawing in Figure 1 shows the molecular structure, which verifies the bridging CO ligands indicated by the IR spectrum. Bridging CO ligands on third-row metals are less commonly

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Table 1. Crystallographic Data and Refinement Information for $[Cp^*(CO)_2Os]_2$

formula	$C_{24}H_{30}O_4Os_2$
formula wt	762.88
temp (K)	293(2)
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	9.792(2)
b (Å)	8.3580(17)
c (Å)	14.374(3)
β (deg)	99.83(3)
V (Å^3)	1159.1(4)
Z	2
μ (mm^{-1})	20.601
λ (Å)	1.541 78
ρ(calcd) (g cm^{-3})	2.186
total no. of rflns	2386
no. of params	142
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0456, wR2 = 0.1019
R indices (all data)	0.0558, wR2 = 0.1076

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(|F_o^2| - |F_c^2|)^2]/\sum[w|F_o^2|^2]\}^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Cp(CO)_2Os]_2$

Os(1)−C(6)	1.855(8)	Os(1)−Cp*[a]	1.923(8)
Os(1)−C(7)	2.043(7)	Os(1)−Os(1)‡ [b]	2.7668(7)
Os(1)−C(7)‡	2.027(8)		
C(6)−Os(1)−C(7)	92.7(3)	C(7)−Os(1)−C(7)‡	94.4(3)
C(6)−Os(1)−C(7)‡	94.2(3)	Os(1)−C(7)−Os(1)‡	85.6(3)

[a] Cp* designates the centroid of the C_5Me_5 ring. [b] The double dagger (‡) indicates that the parameter is related by the symmetry operation $-x$, $-y + 2$, $-z$.

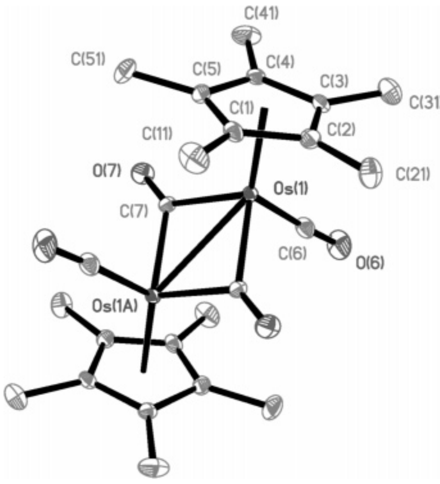
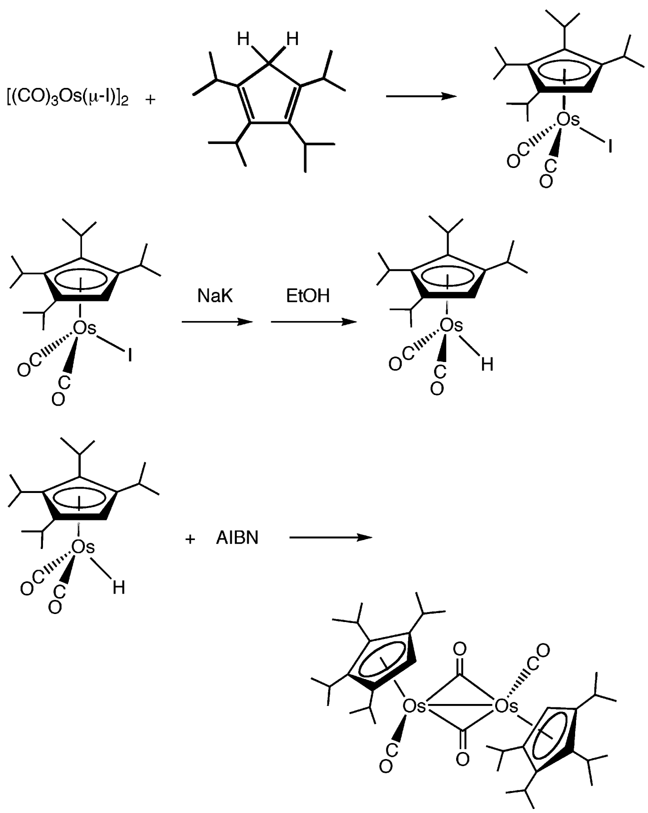


Figure 1. Molecular structure of $[Cp^*(CO)_2Os]_2$ showing 30% probability ellipsoids.

observed compared to first- and second-row complexes, but there is precedent for bridging CO's in Os complexes. For example, the dinuclear complex $Os_2(CO)_9$[18] was shown by IR to have a bridging CO.

The Os−Os bond distance of 2.7668(7) Å found for $[Cp^*(CO)_2Os]_2$ is longer than that found in the hydride-bridged complex[19] $[Cp^*(CO)(\mu\text{-}H)Os]_2$ (2.6733(6) Å) but shorter than that found in $[Cp^*Br(\mu\text{-}Br)Os]_2$ (2.970(1) Å), which has both terminal and bridging Br ligands.[20] Girolami and co-workers reported the crystal structure of $[Cp^*Os(\mu\text{-}NO)]_2$, which has bridging nitrosyl ligands and an Os−Os distance of 2.539(1) Å.[21]

Scheme 2



Synthesis of $[(^iPr_4C_5H)(CO)_2Os]_2$. Complexes with bulky Cp ligands are often used to prepare metal complexes that have significantly different steric and electronic properties compared to those of their Cp analogues.[22] We have begun to study the kinetics of carbon-to-metal hydrogen atom transfers.[3] In these experiments, flash photolysis of a metal−metal dimer such as $[Cp(CO)_2Os]_2$ is carried out in the presence of a hydrocarbon (e.g., 1,4-cyclohexadiene) capable of donating a hydrogen atom to the photochemically generated metal-centered radical. Our experiments have been carried out using transient infrared spectroscopy, and the preferred solvents are saturated hydrocarbons, to avoid absorbances that more polar solvents often have. Considering the poor solubility of $[Cp^*(CO)_2Os]_2$ in hexane, we sought to prepare highly alkylated Cp derivatives that might exhibit enhanced solubility in hydrocarbons. Hanusa and co-workers synthesized a variety of interesting calcium complexes that have cyclopentadienyl ligands substituted by four isopropyl groups,[23,24] and this ligand appeared to offer the characteristics we sought for our osmium complexes.

$[(^iPr_4C_5H)(CO)_2Os]_2$ was prepared by the reactions shown in Scheme 2. Reaction of tetraisopropylcyclopentadiene with $[(CO)_3Os(\mu\text{-}I)]_2$ for 72 h at 180 °C in toluene led to the isolation of the osmium iodide complex $(^iPr_4C_5H)(CO)_2OsI$ in good yield. This reaction is analogous to that used for the preparation of $Cp(CO)_2OsI$ and $Cp^*(CO)_2OsI$.[7] This iodide complex is con-

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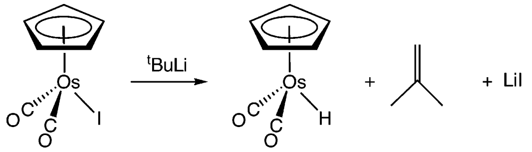
verted to the hydride complex (^{i}Pr$_4$C$_5$H)(CO)$_2$OsH in excellent yield through reaction with NaK in THF followed by treatment with EtOH. Reduction of (^{i}Pr$_4$C$_5$H)(CO)$_2$OsI with NaK produces (^{i}Pr$_4$C$_5$H)(CO)$_2$Os$^-$K$^+$, which exhibits broad IR absorptions for CO ligands at 1864 and 1768 cm^{-1} in THF. Protonation of this osmium anion by EtOH results in the formation (^{i}Pr$_4$C$_5$H)(CO)$_2$OsH. The dimer [(^{i}Pr$_4$C$_5$H)(CO)$_2$Os]$_2$ results from reaction of (^{i}Pr$_4$C$_5$H)(CO)$_2$OsH with AIBN in hexane, analogous to the synthesis of [Cp*(CO)$_2$Os]$_2$ (eq 2).

The IR bands for the CO ligands of [(^{i}Pr$_4$C$_5$H)(CO)$_2$Os]$_2$ at 1919 and 1718 cm^{-1} in CH$_2$Cl$_2$ are about 10 cm^{-1} higher in energy compared to those of [Cp*(CO)$_2$Os]$_2$, and they indicate the presence of bridging CO ligands, as found in [Cp*(CO)$_2$Os]$_2$. The dimer [(^{i}Pr$_4$C$_5$H)(CO)$_2$Os]$_2$ is much more soluble in hexane than is [Cp*(CO)$_2$Os]$_2$. The ^{13}C NMR spectrum of [(^{i}Pr$_4$C$_5$H)(CO)$_2$Os]$_2$ exhibits resonances at δ 114.1 and 105.5 for the Cp ring carbons that are substituted by ^{i}Pr groups, and a resonance at δ 78.3 is assigned to the CH of the ^{i}Pr$_4$C$_5$H ring. A very broad resonance at δ 205.1 is observed for the CO ligands. This chemical shift is significantly downfield of the resonances normally observed for terminal CO ligands bound to Os: e.g., δ 184.4 that we found for (^{i}Pr$_4$C$_5$H)(CO)$_2$OsH, δ 185.5 reported[25] for [Cp(CO)$_2$Os]$_2$, and δ 186.3 reported for Cp*(CO)$_2$Os(CH$_3$).[9] The broad resonance could be due to exchange between terminal and bridging CO ligands. Efforts to freeze out this process at lower temperatures were not successful; the CO ligands were not observed in the ^{13}C NMR spectrum at −35 °C, due to the low solubility of the complex at this temperature. Photochemical and other reactivity studies of this complex are currently being carried out. Crystals of [(^{i}Pr$_4$C$_5$H)(CO)$_2$Os]$_2$ were obtained but appear to be twinned; therefore, a crystal structure could not be obtained.

Synthesis of Cp(CO)$_2$OsH. Graham and co-workers reported the isolation of Cp(CO)$_2$OsH in 31% yield from the reaction of (CO)$_4$OsBr$_2$ with TlCp at 220 °C.[26] The remarkable stability of this complex is evident from the high temperatures used in its synthesis. Herrmann and co-workers reported[6] a 48−50% yield of Cp(CO)$_2$OsH from the reaction of Na(C$_5$H$_5$) with [(CO)$_3$OsCl$_2$]$_2$. We found that Cp(CO)$_2$OsH can be isolated in 70% yield from the reaction of Cp(CO)$_2$OsI with ^{t}BuLi (eq 3). It was formed in 50−60% yield from reduction of Cp(CO)$_2$OsI with NaK, followed by treatment with EtOH, analogous to that described above for (^{i}Pr$_4$C$_5$H)(CO)$_2$OsH.



(3)

Synthesis of Cp*(CO)$_2$OsH. Graham and co-workers found that Cp*(CO)$_2$OsH could be isolated in 65% yield from the reaction of Os$_3$(CO)$_{12}$ with excess pentamethylcyclopentadiene at 200 °C. We found that photolysis of the osmium butyl complex Cp*(CO)$_2$OsBu leads to Cp*(CO)$_2$OsH, which was isolated in 94% yield.[27] By analogy to the preparation of Cp(CO)$_2$OsH discussed above, reaction of Cp*(CO)$_2$OsI with ^{t}BuLi or with NaK, followed by treatment with EtOH, provides a convenient route to Cp*(CO)$_2$OsH (55−65% isolated yield).

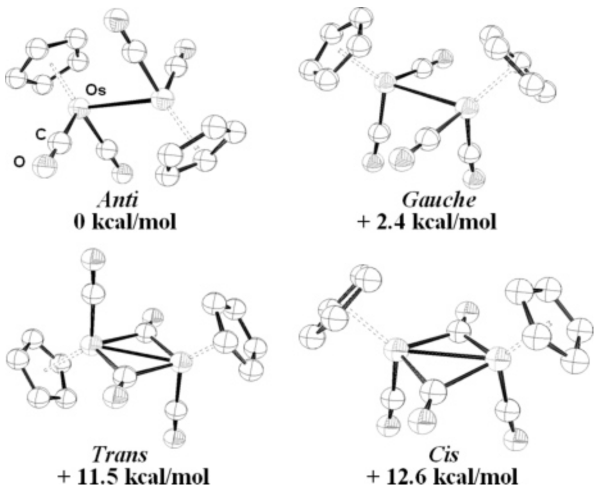


Figure 2. Calculated relative energies (ΔG) of [Cp(CO)$_2$Os]$_2$ at 298.15 K.

Computational Studies on Isomers of [Cp(CO)$_2$Os]$_2$. Numerous studies have examined the factors that influence the relative energetics of isomers of [Cp(CO)$_2$Fe]$_2$ and [Cp(CO)$_2$Ru]$_2$. The iron complex [Cp(CO)$_2$Fe]$_2$ exists mainly in the form with bridging CO ligands, while [Cp(CO)$_2$Ru]$_2$ is found to have the all-terminal and bridging forms in equilibrium. In general, the bridging forms are more stable than the terminal isomers. These equilibria are affected by temperature, solvent, and pressure, and an excellent discussion of these studies is provided in Bitterwolf's review.[15]

As discussed above, the IR spectrum of the [Cp(CO)$_2$Os]$_2$ dimer showed no evidence for a bridging CO ligand, indicating that [Cp(CO)$_2$Os]$_2$ only exists in the terminal forms, in sharp contrast to its iron and ruthenium analogues. The relative energies of geometrical isomers of [Cp(CO)$_2$Os]$_2$ were evaluated using DFT calculations at B3LYP level of theory. Consistent with the experimental observations, the structures with all terminal CO ligands (anti and gauche) have much lower energies than the bridging structures (cis and trans).

The calculated Os−Os bond distances in the anti and gauche isomers (both 2.877 Å) are slightly longer than those in the cis and trans isomers (2.798 and 2.793 Å). The bond lengths between the osmium center and the carbon atoms of the bridging CO groups in the cis and trans forms are longer than the Os−CO bond lengths of the terminal CO groups (2.068 and 2.068 Å vs 1.873 and 1.866 Å), a trend previously observed in the CO-bridged Fe and Ru dimers.[28] Since the computed energy difference between two nonbridged isomers, the anti and gauche rotamers, is only 2.4 kcal/mol (Figure 2), it is expected that both isomers would be present in solution at room temperature. The calculated IR CO absorption frequencies for the anti isomer are 1938 cm^{-1} (1597) and 1967 cm^{-1} (1121); those for the gauche isomer are 1941 cm^{-1} (1039), 1943 cm^{-1} (258), 1968 cm^{-1} (526), and 2010 cm^{-1} (1061) (relative intensities shown in parentheses; see Figure 3).

The IR spectrum of [CpOs(CO)$_2$]$_2$ in hexane has two major bands at 1932 and 1969 cm^{-1} along with a less intense band at 2015 cm^{-1}. The predicted IR spectra of the anti and gauche rotamers in a ratio of 50:1 (derived from the energy difference of 2.4 kcal/mol at 298.15 K) matches well with the experimental spectrum (Figure 4). In THF, a much higher intensity was

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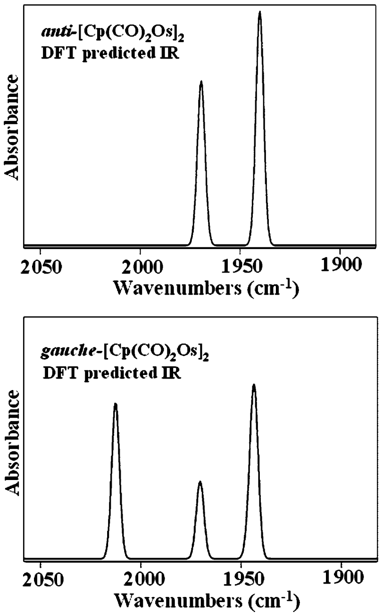

Figure 3. Computed (DFT) IR bands (CO) of $[CpOs(CO)_2]_2$.

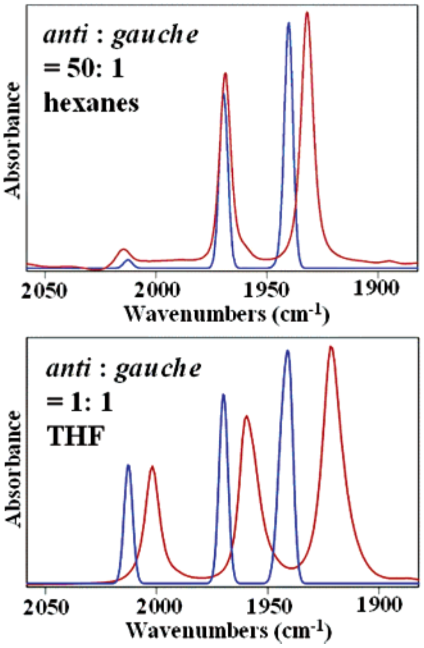

Figure 4. Experimentally measured and computed IR spectra of $[CpOs(CO)_2]_2$: (top) calculated for 50:1 anti:gauche (blue) and experimentally observed in hexane solution (red); (bottom) calculated for 1:1 anti:gauche (blue) and experimentally observed in THF solution (red).

observed for the high-energy band, indicating a larger amount of the gauche isomer in this more polar solvent. A ratio of 1:1 anti:gauche was estimated from the relative intensities in THF solution (see Figure 4). The more polar gauche isomer is significantly stabilized in the more polar solvent. Manning studied the IR spectra of the iron dimer $[CpFe(CO)_2]_2$ in several solvents and found an increasing cis:trans ratio as the solvent polarity was increased.[29] Similar observations were made by McArdle and Manning for the ruthenium analogue $[CpRu(CO)_2]_2$.[30]

Computational Studies on Isomers of $[Cp^*(CO)_2Os]_2$. We have calculated the molecular structure of *trans*-$[Cp^*(CO)_2Os]_2$ and compared the result with the geometric parameters determined by crystallography. The computed bond lengths and angles are all in good agreement with the experimental data (Table 3).

Table 3. Comparison of Crystallographic and Computational Values for Geometric Parameters of *trans*-$[Cp^*(CO)_2Os]_2$

bond length (Å) or angle (deg)	exptl (X-ray)	calcd
Os−Os	2.7668(7)	2.817
Cp*−Os[a]	1.928(7)	1.993
Os−CO	1.855(8)	1.863
C−O	1.151(10)	1.170
Os−CO(b)[b]	2.043(7)	2.068
C−O(b)	1.197(9)	1.196
Os−C(b)−Os	85.7(3)	85.8

[a] The distance from Os to the centroid of the Cp* ring. [b] (b) represents the bridging CO ligand.

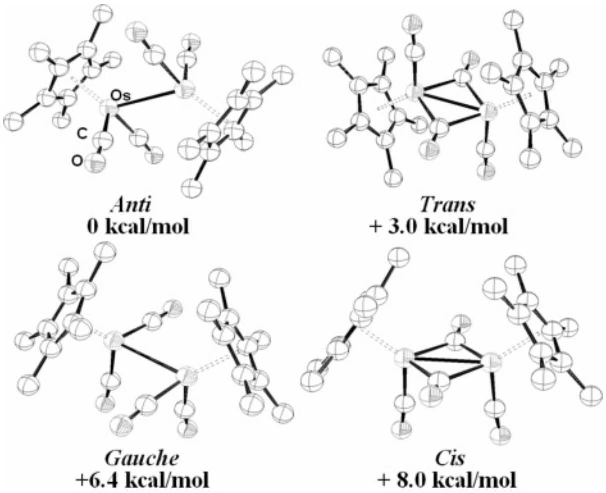

Figure 5. Calculated relative energies (Δ*G*) of $[Cp^*(CO)_2Os]_2$ at 298.15 K.

The relative energies of geometrical isomers of $[Cp^*(CO)_2Os]_2$ were also evaluated. The bridged trans isomer (which is experimentally observed) was computed to lie 3 kcal/mol higher than that of the nonbridged anti isomer (Figure 5). The bridged and nonbridged isomers with the Cp* ligands in cis and gauche configurations are at higher energy, presumably due to the steric repulsion of the Cp* ligands being close to each other. The smaller range of energies computed for these Cp* complexes compared to those of the Cp system above suggests that the Cp* ligands make the relative energies of the unbridged and bridged isomers closer. To further identify the origin of this effect of Cp* ligands, we calculated the energies of $[(C_5(CF_3)_5)(CO)_2Os]_2$, a hypothetical Os dimer with a perfluoro Cp* ligand. The results show that the nonbridged anti isomer is 10.1 kcal/mol more stable than the trans isomer. To the extent that the steric factors of Cp* and $(C_5(CF_3)_5)$ are similar,[31] the major contribution that causes the difference in energy between the anti and trans isomers is likely the result of an electronic effect.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques or in a Vacuum Atmospheres drybox. ^1H NMR chemical shifts were referenced to the residual proton peak of CD_2Cl_2 at δ 5.32. Elemental analyses were carried out by Atlantic Microlab Inc.

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(Norcross, GA). NMR spectra were recorded on a Bruker Avance spectrometer (400 MHz for ^1H). THF, diethyl ether, toluene, and hexanes were dried by passage through drying columns made by Glasscontour, Inc. (www.glasscountour.com). CH_2Cl_2 was distilled from CaH_2. Tetraisopropylcyclopentadiene,[23] $CpOs(CO)_2I$,[7] and $Cp^*Os(CO)_2I$[7] were synthesized according to published procedures. NaK alloy was prepared by placing Na and K (22% Na to 78% K mole ratio) in a flask under argon and heating until a liquid was formed. It was filtered through a coarse frit and stored in a drybox. Other reagents were obtained from Aldrich and used without further purification.

Preparation of $[Cp(CO)_2Os]_2$. $CpOs(CO)_2I$ (1.00 g, 2.28 mmol) was dissolved in THF (50 mL) under Ar, and NaK alloy (0.32 g) was added. The mixture was stirred at room temperature, and the reaction was monitored by IR spectra. After 1 h, all of the starting $CpOs(CO)_2I$ was consumed. The excess NaK was removed by filtration to give a yellow solution. The solvent was evaporated, and the resulting yellow residue was extracted with CH_2Cl_2 (3 × 10 mL). After the CH_2Cl_2 was removed, $[CpOs(CO)_2]_2$ (0.67 g, 1.08 mmol, 94% yield) was obtained as an air-stable yellow compound. It is necessary to stop the reaction as soon as the starting $CpOs(CO)_2I$ is consumed, since long reaction times can reduce the yield because $[CpOs(CO)_2]_2$ reacts with NaK to form $[Cp(CO)_2Os]^-K^+$. ^1H NMR (THF-d_8): δ 5.45 (s, C_5H_5). IR (hexane): 2015 (w), 1969 (s), 1932 (s) cm^{-1}. IR (CH_2Cl_2): 2003 (m), 1960 (s), 1920 (s) cm^{-1}. IR (THF): 2002 (s), 1959 (s), 1921 (s) cm^{-1}.

Preparation of $[Cp^*(CO)_2Os]_2$. (a) Preparation in THF. $Cp^*Os(CO)_2H$ (0.20 g, 0.52 mmol) and AIBN (0.17 g, 1.03 mmol) were charged into a 100 mL Schlenk tube, and THF (25 mL) was vacuum-transferred into the tube. The Schlenk tube was sealed and heated to 70 °C. The solution was stirred at this temperature for 36 h and then cooled to room temperature. The solvent was removed, and the resulting residue was washed with acetone and dried under vacuum at room temperature for several hours to give $[Cp^*Os(CO)_2]_2$ (0.090 g, 0.12 mmol, 46% yield) as an air-stable yellow solid. This solid is almost insoluble in hexane or acetone and slightly soluble in CH_2Cl_2 or THF.

(b) Preparation in Hexane. $Cp^*Os(CO)_2H$ (18.5 mg, 0.048 mmol) and AIBN (8.0 mg, 0.048 mmol) were charged into a 50 mL Schlenk tube, and hexane (15 mL) was added to the tube. The Schlenk tube was sealed and heated to 80 °C for 4 days. During this time, the solution turned yellow, and a yellow solid precipitated from the solution. After the mixture was cooled to −10 °C overnight, the yellow solid was collected by filtration, washed with acetone, and dried under vacuum at room temperature to give $[Cp^*Os(CO)_2]_2$ (9.2 mg, 0.012 mmol, 50% yield). A crystal of $[Cp^*(CO)_2Os]_2$ was grown by layering hexane over a CH_2Cl_2 solution of $[Cp^*Os(CO)_2]_2$ at −10 °C. ^1H NMR (CD_2Cl_2): δ 1.94 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 211.1 (CO), 99.1 (C_5Me_5), 8.6 (C_5Me_5). IR (CH_2Cl_2): 1909 (s), 1708 (s) cm^{-1}. IR (THF): 1911 (s), 1718 (s) cm^{-1}. IR (toluene): 1910 (s), 1719 (s) cm^{-1}.

Collection and Reduction of X-ray Data. X-ray data sets were collected on a crystal of $[Cp^*Os(CO)_2]_2$. A yellow prism of $[Cp^*Os(CO)_2]_2$ was coated with Vaseline and sealed inside a glass capillary. Diffraction data were obtained using an Enraf-Nonius CAD-4 diffractometer with copper radiation, and a graphite monochromator indicated monoclinic symmetry with systematic absences consistent with space group $P2_1/n$. Crystal data and information about the data collection and refinement are provided in Table 1.

Determination and Refinement of the Structure. The structures were solved by standard heavy-atom Patterson methods.[32] In the least-squares refinement,[33] anisotropic temperature parameters were used for all the non-hydrogen atoms. The hydrogen atoms were placed at calculated positions and allowed to "ride"[33] on the atom to which they were attached. A common isotropic thermal parameter was refined for all the hydrogen atoms. A Fourier absorption correction was applied.

Preparation of $(^iPr_4C_5H)(CO)_2OsI$. $Os_3(CO)_{12}$ (0.90 g, 0.99 mmol) and I_2 (0.38 g, 1.50 mmol) were charged into a 100 mL glass bulb with a Teflon valve, and toluene (50 mL) was added. After the mixture was degassed under vacuum, the bulb was sealed and heated to 180 °C for 24 h. The mixture was then cooled to room temperature, and tetraisopropylcyclopentadiene (1.17 g, 4.99 mmol) was added under Ar. The mixture was degassed by pumping on the solution, and the bulb was sealed and heated to 180 °C again. After 72 h, the reaction mixture was cooled and the solvent was removed. The resulting residue was recrystallized from hexane to obtain $(^iPr_4C_5H)(CO)_2OsI$ (1.17 g, 1.93 mmol, 65% yield) as an air-stable yellow solid. IR (toluene): 2019 (s), 1965 (s) cm^{-1}. IR (THF): 2017 (s), 1962 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 5.19 (s, 1H, C_5H), 2.89 (sept, 2H, $CHMe_2$, J = 7 Hz), 2.87 (sept, 2H, $CHMe_2$, J = 7 Hz), 1.39 (d, 12H, $CHMe_2$, J = 7 Hz), 1.27 (d, 6H, $CHMe_2$, J = 7 Hz), 1.19 (d, 6H, $CHMe_2$, J = 7 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 179.3 (CO), 110.9 and 109.4 (Cp ring C-^iPr), 77.5 (Cp ring CH), 25.6, 25.2, 24.9, and 23.9 ($CHMe_2$), 24.5 ($CHMe_2$). Anal. Calcd for $C_{19}H_{29}O_2OsI$: C, 37.62; H, 4.82. Found: C, 37.61; H, 4.77.

Preparation of $(^iPr_4C_5H)(CO)_2OsH$. $(^iPr_4C_5H)(CO)_2OsI$ (0.28 g, 0.46 mmol) was dissolved in THF (20 mL), and then NaK (0.25 g) was added. After the mixture was stirred at room temperature for 2 h, the excess NaK was removed by filtration. Then EtOH (1 mL) was added to the solution, and the mixture was stirred at room temperature for 5 min. The solvent was removed, and the resulting residue was extracted with hexane (3 × 5 mL). The extracts were combined and filtered through a small amount of silica gel. The hexane was removed to obtain $(^iPr_4C_5H)(CO)_2OsH$ (0.22 g, 0.46 mmol, 100% yield) as a white solid. IR (THF): 2071 (w, Os−H), 1994 (s, CO), 1930 (s, CO) cm^{-1}. IR (CH_2Cl_2): 2072 (w, Os−H), 1993 (s, CO), 1926 (s, CO) cm^{-1}. IR (hexane): 2073 (w, Os−H), 2004 (s, CO), 1943 (s, CO) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 5.02 (s, 1H, C_5H), 2.81 (sept, 2H, $CHMe_2$, J = 7 Hz), 2.72 (sept, 2H, $CHMe_2$, J = 7 Hz), 1.37 (d, 6H, $CHMe_2$, J = 7 Hz), 1.36 (d, 6H, $CHMe_2$, J = 7 Hz), 1.22 (d, 6H, $CHMe_2$, J = 7 Hz), 1.19 (d, 6H, $CHMe_2$, J = 7 Hz), −14.22 (s, 1H, OsH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 184.4 (CO), 111.5 and 109.5 (Cp ring C-^iPr), 73.4 (Cp ring CH), 26.4, 25.9, 25.4, and 25.0 ($CHMe_2$), 25.2 ($CHMe_2$).

Preparation of $[(^iPr_4C_5H)(CO)_2Os]_2$. $(^iPr_4C_5H)(CO)_2OsH$ (0.73 g, 1.52 mmol) was dissolved in hexane (60 mL), and AIBN (0.35 g, 2.13 mmol) was added. The solution was sealed into a 100 mL glass bulb with a Teflon valve and heated to 80 °C for 72 h. Yellow crystals precipitated. The solution was concentrated to 30 mL, and $[(^iPr_4C_5H)(CO)_2Os]_2$ (0.37 g, 0.39 mmol, 51% yield) was collected by filtration as a air-stable yellow solid. IR (CH_2Cl_2): 1919 (s), 1718 (s) cm^{-1}. IR (THF): 1922 (s), 1726 (s) cm^{-1}. IR (hexane): 1928 (s), 1731 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.48 (s, 2H, C_5H), 2.88−2.93 (m, 8H, $CHMe_2$), 1.42 (d, 12H, $CHMe_2$, J = 7 Hz), 1.37 (d, 12H, $CHMe_2$, J = 7 Hz), 1.23 (d, 12H, $CHMe_2$, J = 7 Hz), 1.02 (d, 12H, $CHMe_2$, J = 7 Hz). ^1H NMR (C_6D_6): δ 4.70 (s, 2H, C_5H), 3.10 (sept, 4H, $CHMe_2$, J = 7 Hz), 2.88 (sept, 4H, $CHMe_2$, J = 7 Hz), 1.57 (d, 12H, $CHMe_2$, J = 7 Hz), 1.27 (d, 12H, $CHMe_2$, J = 7 Hz), 1.24 (d, 12H, $CHMe_2$, J = 7 Hz), 1.09 (d, 12H, $CHMe_2$, J = 7 Hz). ^1H NMR (THF-d_8): δ 4.56 (s, 2H, C_5H), 2.96 (sept, 4H, $CHMe_2$, J = 7 Hz), 2.94 (sept, 4H, $CHMe_2$, J = 7 Hz), 1.45 (d, 12H, $CHMe_2$, J = 7 Hz), 1.39 (d, 12H, $CHMe_2$, J = 7 Hz), 1.25 (d, 12H, $CHMe_2$, J = 7 Hz), 1.05 (d, 12H, $CHMe_2$, J = 7 Hz). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 205.1 (br, CO), 114.1 and 105.5 (Cp ring C-^iPr), 78.3 (Cp ring CH), 24.5, 23.5, 22.6, and 19.8 ($CHMe_2$), 21.9 ($CHMe_2$). Anal. Calcd for $C_{38}H_{58}O_4Os_2$: C, 47.58; H, 6.09. Found: C, 47.61; H, 6.15.

Preparation of $Cp(CO)_2OsH$. $CpOs(CO)_2I$ (1.02 g, 2.32 mmol) was charged into a 200 mL Schlenk tube, and Et_2O (100 mL) was

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added into the tube under Ar. The solution was cooled to −78 °C, and ^{t}BuLi (1.7 M solution in pentane, 4.1 mL, 6.97 mmol) was added dropwise into the solution over about 10 min. The mixture was stirred at −78 °C for 2 h and then slowly warmed to room temperature. After it was stirred at room temperature for 30 min, the mixture was cooled to −78 °C again and 5 mL of ethanol was added to kill off the excess ^{t}BuLi. The solvent was removed, and the resulting residue was extracted with CH_2Cl_2 (3 × 5 mL). The extracts were combined and filtered through a small plug of silica gel. After the CH_2Cl_2 was removed, a brown oil was obtained. The oil was purified by vacuum sublimation at room temperature, and $CpOs(CO)_2H$ (0.51 g, 1.63 mmol, 70% yield) was obtained as a white solid at −78 °C, which melted to become a colorless oil at room temperature. ^1H NMR (CD_2Cl_2): δ 5.46 (s, 5H, C_5H_5), −14.49 (s, 1H, OsH). ^1H NMR (C_6D_6): δ 4.48 (s, 5H, C_5H_5), −14.12 (s, 1H, OsH). ^1H NMR (THF-d_8): δ 5.52 (s, 5H, C_5H_5), −14.47 (s, 1H, OsH). IR (hexane): 2089 (w, Os−H), 2021 (s, CO), 1960 (s, CO) cm^{-1}. IR (THF): 2081 (w, Os−H), 2009 (s, CO), 1943 (s, CO) cm^{-1}. IR (CH_2Cl_2): 2083 (w, Os−H), 2011 (s, CO), 1944 (s, CO) cm^{-1}.

An alternative way to prepare $Cp(CO)_2OsH$ is to reduce $Cp(CO)_2OsI$ with NaK in THF and then protonate the resulting Os anion, as described in the synthesis of $(^iPr_4C_5H)(CO)_2OsH$. Isolated yields of 50−60% were obtained using this procedure.

Preparation of $Cp^*(CO)_2OsH$. $Cp^*Os(CO)_2H$ was synthesized through the reaction of $Cp^*Os(CO)_2I$ with ^{t}BuLi in ether, using a procedure similar to that described above for the preparation of $CpOs(CO)_2H$. The final purification was carried out by vacuum sublimation at 50 °C. From $Cp^*Os(CO)_2I$ (1.02 g, 2.00 mmol), $Cp^*Os(CO)_2H$ (0.46 g, 1.20 mmol, 60% yield) was obtained as a white solid. ^1H NMR (CD_2Cl_2): δ 2.20 (s, 15H, C_5Me_5), −14.08 (s, 1H, Os*H*). IR (hexane): 2060 (w, Os−H), 2000 (s, CO), 1942 (s, CO) cm^{-1}. IR (CH_2Cl_2): 2054 (w, Os−H), 1989 (s, CO), 1923 (s, CO) cm^{-1}. IR (THF): 2052 (w, Os−H), 1991 (s, CO), 1928 (s, CO) cm^{-1}.

Computational Details. Density functional theory (DFT) calculations on the osmium complexes were performed using the Gaussian 03 program (Revision C.02).[34] The B3LYP gradient corrected exchange hybrid DFT method[35] was employed. Geometry optimizations were performed using the default convergence criteria without any geometric constraints. The LANL2DZ ECP basis set[36] was applied for the osmium atoms. An all-electron Pople basis set, 6-31G(d),[37] was employed for the rest of the C, H, and O atoms. Frequency calculations were used to characterize the stationary points as minima or transition-state structures, as well as to determine zero-point energies (ZPEs). The reported frequencies are scaled by 0.96.[38]

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Supporting Information Available: Crystallographic data as a CIF file and tables giving further details of the DFT computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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