J. Am. Chem. Soc. **1996,** *118,* 8916−8919

Transition Metal Polyhydride Complexes. 8. Pentahydrido(cyclopentadienyl)osmium(VI)

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Received April 17, 1996[⊗]

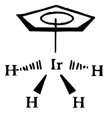
Abstract: The recent synthesis of (pentamethylcyclopentadienyl)osmium(VI) pentahydride (Cp^*OsH_5) completes the series of high-oxidation-state cyclopentadienyl metal polyhydrides. A single hydride resonance in the proton NMR spectrum indicated that the complex contained either five equivalent hydride ligands or inequivalent hydrides in rapid exchange. Vibrational studies were inconclusive as to whether the molecule adopted a C_{5v} (pseudo-pentagonal-pyramid with the Cp ring occupying the axial position) or a pseudo-C_{4v} (pseudo-octahedral with the Cp ring considered as occupying one site) orientation in the ground state. In this study, *ab initio* calculations with effective core potentials were performed on pentahydrido(cyclopentadienyl)osmium(VI), $CpOsH_5$, to determine its structure, vibrational spectrum, and rearrangement mechanism. Geometry optimizations at the Hartree−Fock (HF) and second-order Møller−Plesset (MP2) levels of theory and energy calculations at the MP3, configuration interaction singles and doubles (CISD), coupled cluster singles and doubles (CCSD), and coupled cluster singles and doubles with perturbative estimate of triple excitations (CCSD(T)) levels place the pseudo-C_{4v} structure lower in energy than the C_{5v} structure. When compared to the experimental results, the calculated frequencies confirm that the pseudo-C_{4v} geometry is the experimentally observed conformation. The topography of the MP2 potential energy surface supports the notion of a highly fluxional pseudo-C_{4v} geometry which exchanges hydride ligands through a Bailar or trigonal-twist mechanism without passing through the C_{5v} geometry.

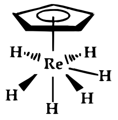
Introduction

As the smallest possible ligand, the hydride ligand has intrigued inorganic and organometallic chemists for some time. Many polyhydride complexes possess unusual structures or interesting reactivity including important catalysis such as the hydrogenation of alkenes. Due to the small size and ability of the ligand to move easily between binding sites, it is very difficult to characterize the ground state structure except by neutron diffraction, a technique that requires the growth of a large crystal. It is easier in many cases to attempt a theoretical determination of the structure. In a series of papers,[1] this group has shown the reliability of second-order Møller−Plesset (MP2) in determining of the structure of second- and third-row polyhydride complexes.

In 1983, Gilbert and Bergman[2] synthesized an unusual iridium(V) polyhydride, tetrahydrido(pentamethylcyclopentadienyl)iridium(V), [$(C_5Me_5)IrH_4$, **1a**]. The compound possessed one hydride peak in the ^1H NMR spectrum, suggesting that the compound possessed a four-fold orientation of the hydrides about the metal center. The pseudo-C_{4v} orientation of the hydride ligands in this complex was later verified theoretically by Lin and Hall[1e].

In 1986, the related rhenium compound, hexahydrido(pentamethylcyclopentadienyl)rhenium(VII), was synthesized by Herrmann and Okuda.[3] The structure was analyzed using variable temperature NMR techniques. It was found that at high temperatures the hydride ligands exchanged rapidly, but at lower temperatures, the hydride motion could be frozen out to reveal a 5-fold umbrella structure (**1b**). Theoretical calculations[1f] confirm this C_{5v} structure.


1a


1b

In a recent communication, Gross, Wilson, and Girolami[4] reported the synthesis of a new osmium polyhydride, pentahydrido(pentamethylcyclopentadienyl)osmium(VI). This species lies between the above two polyhydride species in this series of isoelectronic high-oxidation-state third-row transition-metal cyclopentadienyl polyhydride complexes. The compound was found to display a singlet in the ^1H NMR spectrum, which persisted even at fairly low temperatures. The relaxation time (T_1) was large enough to eliminate exchange by a nonclassical dihydrogen complex. Attempts to exchange a deuterium atom with a hydride ligand were unsuccessful; therefore, coupling constants could not be determined.

As this complex completes the series above, it is expected that the geometry of the complex would resemble one of its counterparts. The ^1H-NMR data could support an orientation in which all of the hydride ligands occupy equatorial positions around the metal as in a C_{5v} "piano stool" geometry (**2a**). Alternatively, the molecule could assume a highly fluxional pseudo-C_{4v} geometry with four equatorial hydrides and one axial hydride (**2b**). The latter alternative would require a small

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1996.

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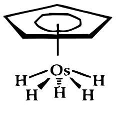
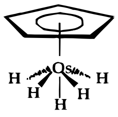


2a



2b

exchange barrier as the hydride motion could not be slowed even at −90 °C, 10° below the low temperature limit of the above rhenium complex.

From the results of infrared and Raman studies, Gross et al.[4] slightly favored the 5-fold structure. This conclusion was reached by comparison of the number of Os-H stretching bands with the number expected from group theory. This method is only qualitative and is often unreliable.

In this work, the relative stability of these two possible structures of the osmium polyhydride has been determined. To support these energy calculations, frequency calculations have been performed and compared to the experimental results. The potential energy surface for the exchange of the hydride ligands has been constructed and the transition state and activation energy of the exchange mechanism have been determined in order to gain better insight into the hydride dynamics in this molecule.

Theoretical Details

All geometries were optimized at both the Hartree−Fock (HF) and MP2 levels of theory. Energies were recalculated at the MP3, configuration interaction singles and doubles (CISD), coupled cluster singles and doubles (CCSD), and coupled cluster singles and doubles with perturbative estimate of the triple excitations (CCSD(T)) levels for comparison. Infrared frequencies were produced using Hartree−Fock calculations at the Hartree−Fock optimized geometry. In order to simplify the calculations, all methyl groups on the Cp* ring were replaced by hydrogens.

Effective core potentials were used for osmium[5] and carbon.[6] A double-ζ basis set with triple-ζ representation of the d-functions was employed on the osmium center (541/651/211). The $(n + 1)$s and $(n + 1)$p orbitals of the metal have been represented in accordance with recent studies showing the importance of these basis functions.[7] Hydrogen atoms directly bonded to the metal were treated with a triple-ζ basis set (311).[8] A double-ζ basis set was used to represent the carbons (31/31) and hydrogens (31) of the cyclopentadienyl ring.[9]

Calculations for relative stabilities and geometries were performed using the GAMESS-UK[10] package. Frequency calculations were performed using Gaussian 94[11] and scaled by 92%.[12]

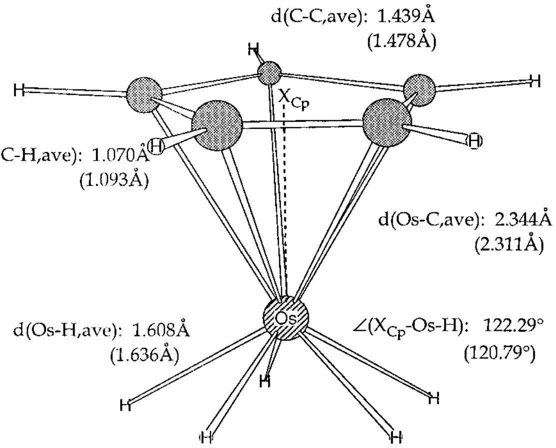


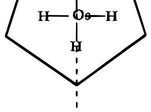
Figure 1. Structural parameters of the C_{5v} complex (**2a**) at the HF (MP2) levels. Distances are given in angstroms (Å). Some of the specified parameters have been averaged from the full geometry optimization.

Calculations were performed on an SGI Power Challenge at the Supercomputer Center of Texas A&M University, on the Chemistry Department's FPS Model 522 and SGI Indigo workstations, and on SGI Indigo workstations of the Institute for Scientific Computation at Texas A&M University. Configuration interaction calculations were performed on the Cray J90 at Texas A&M University. Coupled cluster calculations were performed on the Cray C90 at Cray Research, Inc.

Results

Theoretical Geometries. The C_{5v} structures were optimized at the Hartree−Fock and MP2 levels. The barrier to rotation around the metal center was determined to be 1.4 kcal/mol by varying the dihedral angle ($H_{eq}-Os-X_{Cp}-C$), defined by an equatorial hydride ligand, the metal center, the molecular axis, and one of the carbons of the ring. The lower energy eclipsed conformer (Figure 1) was used for all higher level calculations. The difference between the HF and MP2 calculations involved a decrease in the metal−Cp distance and an increase in the metal-hydride distance. An interesting feature of this complex is the obtuse angle made by the hydride ligands with the molecular axis. Although one would not expect 90° for $\angle(X_{Cp}-Os-H_{eq})$, the angles found in this complex (122.29°, HF; 120.79°, MP2) are considerably smaller than what one would anticipate.

The pseudo-C_{4v} structure was optimized at the Hartree−Fock and MP2 levels of theory with results shown in Figure 2. In an attempt to determine the rotational barrier, the dihedral angle, defined above, was varied from 0 to 18°. Equivalent structures are generated every 18° of rotation, and every 9°, the molecule goes through one of two true C_s orientations corresponding to the eclipsed (**3a**) and staggered (**3b**) conformations. The barrier by this approach is essentially zero. A similar effect is displayed by $CpRhH_4$,[1e] another pseudo-C_{4v} hydride complex. All further calculations were performed using the 0° structure (**3a**) as the minimum. As in the above C_{5v} complex, the M−Cp distance



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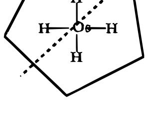

3b

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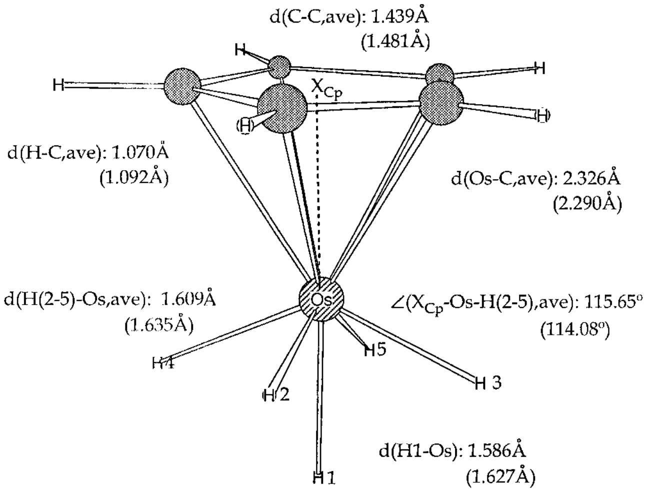

Figure 2. Structural parameters of the pseudo-C_{4v} complex (**2b**) at the HF (MP2) levels. Distances are given in angstroms (Å). Some of the specified parameters have been averaged from the full geometry optimization.

Table 1. Relative Energies (kcal/mol) of the C_{5v} and Pseudo-C_{4v} Geometries of $CpOsH_5$

	ΔE^a, kcal/mol		ΔE^a, kcal/mol
HF//HF	−0.09	CISD//MP2	−3.38
MP2//HF	−8.25	CISD(SCC)//MP2	−4.61
MP2//MP2	−9.12	CCSD//MP2	−5.88
MP3//MP2	−3.73	CCSD(T)//MP2	−6.38

[a] The relative energies are given such that $E(C_{5v}) = 0.0$ kcal/mol. [b] SCC is the Davidson size-consistency correction.

contracted between the HF and MP2 levels, and the M−H distances elongated. The complex also displays a similar obtuse X_{cp}−Os−H_{ax} angle of 114−116°. The obtuse angles in the C_{5v} and pseudo-C_{4v} structures can be explained in terms of a pseudo-Jahn−Teller effect.

In the C_{4v} (C_{5v}) symmetry the $5d_{xz,yz}$, the $6p_{x,y}$, and a hydride combination transform as e (e_1). At X_{Cp}−Os−H_{eq} angles near 90°, as one might expect particularly in the pseudo-C_{4v} structure, the hydride combination can only interact with the 6p orbitals as it lies in the node of the 5d orbitals. By bending to an obtuse angle, the hydride combination can effectively increase its stability by interacting with both the 6p and 5d. This pseudo-Jahn-Teller view has been invoked to explain the obtuse angles in $CpReH_6$[1f].

Relative Energies. The relative energies of the two most likely conformations (**2a**, **2b**) at various levels of theory are listed in Table 1. The significant difference between the HF and MP2 relative energies demonstrates the importance of electron correlation in this system. Optimization of the geometries at the MP2 level increases the stabilization of the pseudo-C_{4v} structure. Higher level perturbation theory (MP3), variational calculations (CISD), and coupled cluster methods (CCSD, CCSD(T)) also show the pseudo-C_{4v} structure (**2b**) as the lowest energy conformer.

Table 2. Experimental (Cp^*OsH_5) and Theoretical ($CpOsH_5$) HF Infrared Frequencies, Intensities, and Symmetry Assignments[a]

expl ν (cm^{-1})	C_{5v} (**2a**) theor ν (cm^{-1})	IR intensity	pseudo-C_{4v} (**2b**) theor ν (cm^{-1})[b]	IR intenensity
(IR/R) 2214 (w)	2147.5 (a_1)	74.6 (m)	2292.3 (a′)	3.7 (w)
(R) 2096 (s)	2164.4 (e_1)	48.8 (m)	2149.3 (a′)	143.3 (s)
(IR) 2083 (s)	2164.4 (e_1)	48.8 (m)	2129.4 (a′)	86.6 (m)
	2181.5 (e_2)	0.0	2128.0 (a″)	102.1 (s)
	2181.5 (e_2)	0.0	2112.8 (a′)	19.6 (w)

[a] Theoretical frequencies have been scaled by 92%. (See ref 12). [b] The symmetry assignment corresponds to the C_s point-group. Symmetry assignments for C_{4v} can be found in Table 4.

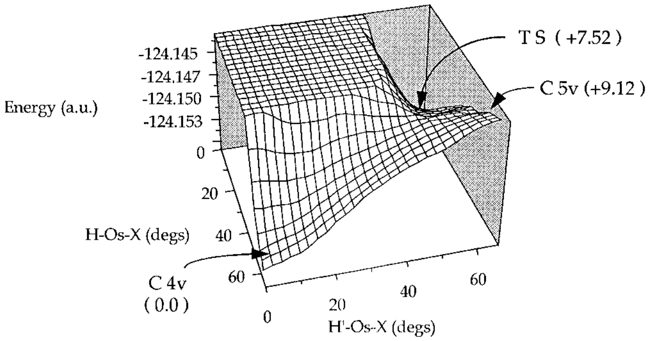

Figure 3. Potential energy surface for the exchange of hydride ligands in $CpOsH_5$.

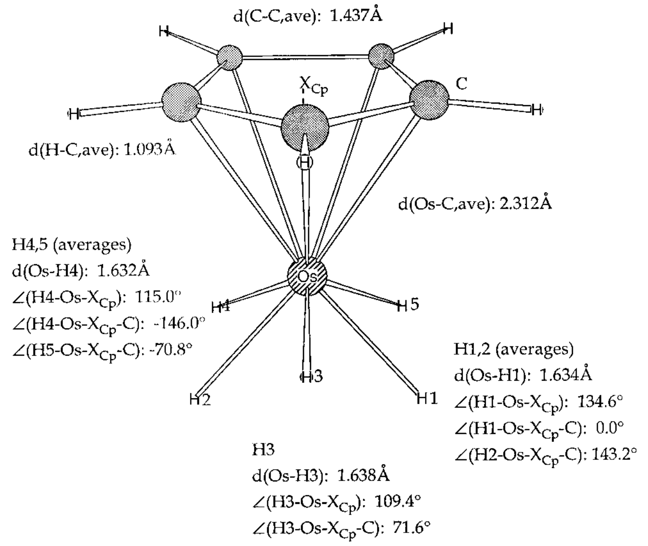

Figure 4. Structure parameters of the transition state for exchange of hydrides in $CpOsH_5$ at the MP2 level. Distances are given in angstroms (Å). Some of the specified parameters have been averaged from the full geometry optimization.

Table 3. Symmetry Decomposition of the Pseudo-C_{4v} (C_s) Normal Modes

theoretical ν (cm^{-1})	C_s assignment	C_{4v} assignment
2149.3	a′	$^3/_2a_1 + {}^1/_2b_1 - {}^1/_2e$
2129.4	a′	$a_1 + b_1 - e$
2128.0	a″	e
2112.8	a′	$^1/_2a_1 - {}^1/_2b_1 - {}^1/_2e$

Frequency Analysis. Frequency calculations on both the C_{5v} and pseudo-C_{4v} geometries at the Hartree−Fock level show only real frequencies. The osmium−hydride stretching frequencies and intensities are tabulated in Table 2. The theoretical spectrum of the C_{5v} structure has closely spaced a_1 and e_1 bands ($\Delta\nu = 17$ cm^{-1}) of similar intensity which would most likely appear as one band in an experimental spectrum. In contrast, the pseudo-C_{4v} spectrum has an a_1 band at 2292.3 cm^{-1} and closely spaced bands of mixed normal modes around 2140 cm^{-1}. Moreover, the calculated intensities show the a_1 band to be weak and the other bands to be strong. The bands are also spaced roughly 150 cm^{-1} apart, closely reproducing the 120 cm^{-1} difference in the experiment. Thus, the calculated bands of the pseudo-C_{4v} structure reproduce both the frequency and intensity pattern of the experiment. The mixed normal modes in the 2140 cm^{-1} band of the pseudo-C_{4v} structure can be decomposed into

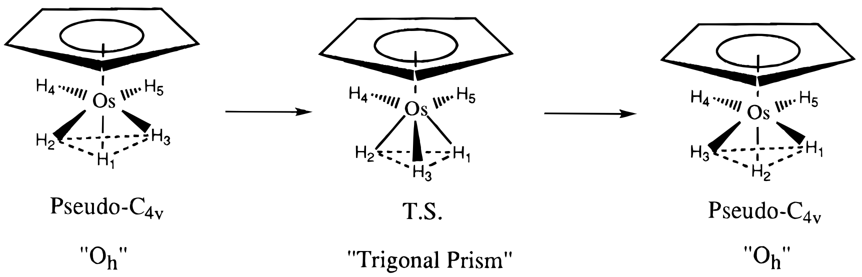

Figure 5. Mechanism of the exchange of hydride ligands in $CpOsH_5$ corresponding the Bailar or trigonal twist.

Table 4. Relative Energies (kcal/mol) of the Pseudo-C_{4v} Structure and the Exchange Transition State Geometry

	$\Delta E^{\ddagger}$, kcal/mol		$\Delta E^{\ddagger}$, kcal/mol
MP2/MP2	7.52	CISD(SCC)//MP2	4.10
MP3/MP2	3.27	CCSD//MP2	4.89
CISD/MP2	3.33	CCSD(T)//MP2	5.18

C_{4v} by transforming the C_s symmetry modes as shown in Table 3. Because the pseudo-C_{4v} modes are close in energy, the small coupling provided by the lower C_s symmetry strongly mixes these modes.

Potential Energy Surface. The potential energy surface (Figure 3) for the interconversion between pseudo-C_{4v} structures was constructed by varying the angles made by the axial hydride ligand (H) and one of the equatorial hydride ligands (H′) with the central axis (X_{Cp}) of the molecule. The surface was sampled by MP2 optimization at several points where these two parameters were fixed between angles of 114° and 180°. From this surface, the transition state of the exchange can be roughly placed at the point at which these hydride ligands are at 135° to the molecular axis. A Jorgensen optimization[13] (MP2 level) at this point provides the geometry of the transition state (Figure 4) which has only one negative force constant. Here, the hydride ligands can be placed into three categories. One ligand (H3) has been displaced roughly 5° out of its equatorial position. Two pairs of hydrides are equivalent at the transition state. The first set (H1,H2) consists of the hydrides used to define the surface. The positions of the latter pair (H4,H5) are roughly unchanged from the pseudo-C_{4v} conformer. The activation barrier for the exchange of hydride ligands was found to be 7.52 kcal/mol at the MP2 level of theory. Energies (Table 4) were calculated at higher levels of theory to introduce additional electron correlation. The small barriers at these higher levels of theory indicate a highly fluxional molecule.

Exchange Mechanism. During the exchange the axial hydride, H1 moves up between H3 and H5 ligands, while the equatorial H2 moves down eventually taking H1's axial place (Figure 5). The exchange mechanism for this system can be thought of as a simple trigonal twist. The H1, H2 and H3 can be viewed as one face of an octahedron, while the H4 and H5 ligands and the cyclopentadienyl ring are the opposite face. As the exchange proceeds, the former face twists so that H2 becomes equivalent to the H1 ligand. At this point, the transition state, the molecule is a pseudo-trigonal prism. The face then continues to twist around back to the octahedral orientation with H1 exchanged with H2. This mechanism is the well-known Bailar[14] or trigonal twist mechanism which is often invoked for rearrangement of tris-chelate "O_h" complexes. The activation barrier for this system is fairly small (Table 4). Given the magnitude of this barrier, it is unlikely that this exchange process would freeze out at temperatures of −90 °C.

Nonclassical Structures. Calculations were also performed on a nonclassical structure in order to determine whether or not two of the hydride ligands could come together to form a dihydrogen ligand from the pseudo-C_{4v} structure, exchange, and return to the pseudo-C_{4v} structure. For these calculations, the hydrogen ligand was constrained to be parallel with the cyclopentadienyl ring and possess an H−H bond distance of 1.0 Å. The optimized structure lay 26.5 kcal/mol higher in energy than the pseudo-C_{4v} structure at the HF level. Previous work in our laboratory has shown that electron correlation at the MP2 and higher levels will only increase this difference.

Conclusion

A theoretical model has been presented for the structure and exchange of hydride ligands in $CpOsH_5$ which is consistent with the experimental results. Frequency calculations, which reproduce the experimental pattern, prove that the true low-energy conformation of Cp^*OsH_5 is the pseudo-C_{4v} geometry. The activation energy for exchange is small such that the pseudo-C_{4v} structure can be expected to be a highly fluxional species down to very low temperatures. The calculations also confirm the experimental conclusion that a nonclassical dihydrogen complex is unrealistic as an intermediate for the exchange process.

Acknowledgment. We would like to thank the National Science Foundation (Grant Nos. CHE91-13634 and 94-23271) and the Robert A. Welch Foundation (Grant No. A-648) for their support. We also thank the Supercomputer Center and the Institute for Scientific Computation at Texas A&M University for the use of their machines. We thank Cray Research, Inc., and Chris Hempel for time on their machine.

JA961265+

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