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Effect of the Spinning Motion of the Dihydrogen Ligand on the Properties of an Elongated Dihydrogen Complex. A Theoretical Study of the *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$ Complex

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Abstract: We present in this paper an electronic structure and quantum nuclear dynamics study of a modeled version of *trans*-$[Os(H\cdots H)Cl(dppe)_2]^+$, an elongated dihydrogen complex classified as being between the fast and slow H_2 spinning limits and whose J(H,D) coupling constant increases on increasing temperature. We have found that the librational potential energy barrier for the motion of the H_2 unit is quite low, in agreement with the spinning regime of the H_2 unit reported from experiment. Additionally, while the electronic structure study does not manage to describe the experimentally reported geometry obtained through neutron diffraction experiments, the quantum nuclear motion study reproduces the experimental findings very satisfactorily. Finally it is seen that only when the librational motion of the H_2 unit is taken into account in an explicit way in the quantum nuclear motion calculations the temperature dependence of the J(H,D) ^{1}H NMR coupling constant is also correctly accounted for.

I. Introduction

Recently, the particular group of transition metal dihydrogen complexes known as “elongated” dihydrogen complexes has received increasing attention in the literature, both at experimental[1−5] and theoretical[6−8] levels. These complexes can be found filling the gap between classical polyhydrides (with H−H distances at or above 1.6 Å) and nonclassical dihydrogen complexes (which have H−H distances below 1.0 Å).[9] As more and more cases of elongated dihydrogen complexes are discovered, it seems that there is an almost continuous gradation in the family of dihydrogen complexes, spanning the range of H−H distances which goes from 0.8 to 1.4 Å, which could even be extended into dihydride complexes as well.

Several authors have tried to explain the existence of elongated dihydrogen complexes and their properties with respect to the temperature dependence of the J(H,D) ^{1}H NMR spectrum coupling constant. About the latter issue, empirical relations exist that relate the values of the J(H,D) coupling constant with H−H distances in elongated dihydrogen complexes.[4b,10,11] In these relations it can be seen that the magnitude of the J(H,D) coupling constant evolves inversely with the H−H distance. As for theoretical works, these complexes are notorious for the problems encountered at the theoretical level when trying to reproduce the geometry of the elongated dihydrogen ligand, even when sophisticated and costly electronic structure calculations are performed.[12]

Recently we have published a theoretical work on the elongated dihydrogen complex $[Ru(H\cdots H)(C_5Me_5)(dppm)]^+$, which was modeled as $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$.[8] This was one of the few cases of stretched dihydrogen complexes for which both a precise structure obtained by neutron diffraction studies and the detailed temperature dependence of the J(H,D) coupling constant data are available.[4a] In that paper we demonstrated that there was no potential energy minimum that could correspond to a stretched dihydrogen complex. Instead, conventional electronic structure studies predicted the existence of a normal dihydrogen ligand with an H−H distance of 0.89 Å. However, the study of the potential energy profile for the H−H stretch revealed that this profile was very anharmonic. Solving the Schrödinger equation for the motion of nuclei on a reduced potential energy surface (PES) of two dimensions, corresponding to the H−H and Ru−H_2 stretches, led to expectation values for the H−H distance in the ground vibrational state of the Ru−H_2 unit of 1.02 Å, sensibly closer to the value reported experimentally (1.10(2) Å). Moreover, when a Boltzmann equilibrium distribution was used to compute the population of the vibrational excited states of the Ru−H_2 unit, the experimental decrease of the J(H,D) coupling constant

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with increasing temperature was very satisfactorily explained in terms of varying populations of excited states with longer H−H distance expectation values. This possibility had been suggested previously by Klooster et al.[4a]

Experimentally, that ruthenium complex has been described as a slow spinning dihydrogen complex. In effect, in our previous work a rotational barrier of 4.23 kcal/mol was calculated for the librational motion of the dihydrogen unit. This relatively high value of the rotational barrier made it possible to disregard the influence of the librational motion of the dihydrogen ligand on the dynamics of the H_2 unit to explain its properties. However, there is another elongated dihydrogen complex reported in the literature that has also been studied by means of neutron diffraction experiments and whose dependence of the *J*(H,D) coupling constant with temperature has been determined, but that has not been characterized as slow spinning dihydrogen complexes, but as an intermediate case. This elongated dihydrogen complex is *trans*-[Os(H···H)Cl(dppe)$_2$]$^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) which is reported to have a long H−H distance (1.22(3) Å).[4b] Presumably, in this complex the energy barrier for the librational motion will be lower than that of the ruthenium complex, in such a way that in this case the degree of freedom describing the librational motion of the dihydrogen unit will no longer be negligible and hence should be taken into account in an explicit way. Additionally, this osmium complex displays a *J*(H,D) coupling constant that depends inversely on temperature when compared to the ruthenium complex. This same behavior has been observed in the complex *trans*-[Os(H···H)H(depe)$_2$]$^+$.[13]

The purpose of this paper is to check if the same physical basis that gives rise to a slowly rotating stretched dihydrogen ligand holds behind the existence of the elongated complex *trans*-[Os(H···H)Cl(dppe)$_2$]$^+$, which has been classified as being between the fast and slow H−H spinning limits. To this aim, the librational motion of the H_2 unit will have to be taken into account explicitly. In this way we will try to theoretically explain the experimentally reported geometry of this complex, as well as trying to find a plausible explanation for the anomalous temperature dependence of the *J*(H,D) coupling constant in the corresponding monodeuterated isotopomer.

II. Calculational Details

As happened in our previous work, two different types of quantum calculations have been performed. Electronic structure calculations have been carried out to locate the stationary points and other interesting points of the potential energy surface (PES), including the evaluation of a sizable part of the PES itself. Additionally, nuclear motion calculations have been done to determine the nuclear motion energy levels and associated wave functions. Both sets of calculations are detailed here.

A. Electronic Structure Calculations. Some modeling has been made on the experimental complex by changing the four phenyl groups in the dppe ligand by hydrogen atoms. As a result, the system that has actually been studied is the cationic complex *trans*-[Os(H_2)Cl($H_2PCH_2CH_2PH_2$)$_2$]$^+$. To solve the electronic Schrödinger equation, the density-functional theory (DFT) methodology has been used.[14] This methodology meets the requirements of high accuracy and reasonable cost needed to construct a moderately large portion of the PES of this complex in a reasonable amount of time. It is worth mentioning that the DFT methodology has been used with great success to study several organometallic systems, including dihydrogen and polyhydride complexes.[6c,d,7,8,15,16] In particular, in our previous work with the ruthenium complex [Ru(H···H)(C_5H_5)($H_2PCH_2PH_2$)]$^+$, the elongation of the dihydrogen unit in the potential energy minimum found by means of DFT was the same as that predicted by coupled cluster calculations, much more expensive in computational terms.[8]

All calculations have been performed within C_2 global symmetry point group without imposing any other geometrical constraints. All electronic structure calculations have been carried out with the GAUSSIAN 94 series of programs,[17] and the DFT formalism was used throughout the entire set of calculations with the three-parameter hybrid functional of Becke and the Lee, Yang, and Parr's correlation functional, which is widely known as Becke3LYP.[18]

To reduce the cost of the computations an effective core operator has been used to replace the inner electrons of the osmium atom.[19] For the 16 outer electrons of the osmium atom, the basis set associated with the pseudopotential of Hay and Wadt with a standard valence double-ζ LANL2DZ contraction was used.[17,19] As for the remainder of atoms of the complex, the standard split-valence 6-31G basis set was chosen,[20a] except for the chlorine and phosphorus atoms, for which the basis set used was 6-31G(d),[20b] and for the hydrogen atoms directly bound to the osmium atom, in which case the 6-31G(p) basis set was used instead.[20a,c]

The stationary points were located using the Schlegel gradient optimization algorithm within a redundant internal coordinate system.[17,21] Forcing the approximate second derivative matrix to contain zero or one single negative eigenvalue, the optimization converges to a minimum or a transition state, respectively.

B. Nuclear Motion Calculations. A significant part of this work needs the nuclear motion levels and wave functions to be calculated. To obtain these, the Schrödinger equation for the motion of nuclei must be solved:

$$\hat{H}_{\text{nuc}}\Psi_{\text{nuc}} = [\hat{T}_{\text{nuc}} + U(\mathbf{R})]\Psi_{\text{nuc}} = E\Psi_{\text{nuc}} \qquad (1)$$

Similar quantum-dynamical studies of other dihydrogen and polyhydride complexes have appeared recently in the literature.[8,22] In eq 1, *U* is the electronic potential energy surface

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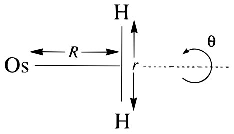
Scheme 1



including the internuclear repulsion energy, obtained within the Born−Oppenheimer approximation from electronic structure calculations. $\boldsymbol{R}$ is a $3N - 6$ component vector that describes a given nuclear arrangement of the molecule. Because of the number of components of $\boldsymbol{R}$, $U(\boldsymbol{R})$ cannot be evaluated completely except for very simple systems. As in our previous work,[8] we will build a reduced PES by considering only a small set of variables for U. As will be seen later, we have performed two different sets of nuclear motion calculations, one based on a two-dimensional and the other on a three-dimensional version of U.

For the two-dimensional calculation the choice of the variables was the same as the one made in our previous work, that is, one variable corresponded to the interatomic distance between the two hydrogens of the H_2 unit of the complex (r), and the other variable to the distance between the osmium atom and the point halfway between both hydrogens of the dihydrogen ligand (R). When three-dimensional calculations were needed, the third variable was the phase of the librational motion of the dihydrogen ligand (θ). The schematic version of the choice of variables is presented in Scheme 1.

In both the two- and three-dimensional versions of the nuclear motion calculations all the variables considered for U behave as orthogonal coordinates. The two-dimensional calculations presented in this paper are in all ways analogous to those presented in our previous work,[8] and for the sake of conciseness the corresponding methodological details will be omitted here. Nevertheless we present here the details corresponding to the three-dimensional calculations, which are novel to this work.

The Hamiltonian of the system when the three chosen variables are considered is the following one:

$$\hat{H}_{\mathrm{nuc}}(r,R,\theta) = -\frac{\hbar^2}{2\mu_r}\left[\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r}\right] - \frac{\hbar^2}{2\mu_R}\left[\frac{\partial^2}{\partial R^2}\right] - \frac{\hbar^2}{2I_{\mathrm{HH}}}\left[\frac{\partial^2}{\partial \theta^2}\right] + V(r,R,\theta) \quad (2)$$

which is essentially the expression of a Hamiltonian operator in cylindrical coordinates. I_{HH} is the inertia momentum of the dihydrogen ligand, and μ_r and μ_R refer to the reduced masses for the motion along the r and R coordinates respectively, which are calculated as follows:

$$\frac{1}{\mu_r} = \frac{1}{m_{\mathrm{H(A)}}} + \frac{1}{m_{\mathrm{H(B)}}}$$
$$\frac{1}{\mu_R} = \frac{1}{m_{\mathrm{H}_2}} + \frac{1}{m_{[\mathrm{OsCl(H_2PCH_2CH_2PH_2)_2}]}} \quad (3)$$

Note that $V(r,R,\theta)$ is the three-dimensional version of the complete potential energy hypersurface of the complex under study. An identical Hamiltonian has been used before to study the quantum exchange coupling in polyhydride transition metal complexes.[22b]

After the Hamiltonian has been defined, eq 1 needs to be solved to determine eigenvalues and eigenfunctions of the system. Due to the fact that the number of dimensions involved in the calculation is considerable, we have opted for using a discrete variable representation (DVR)[23] approach instead of a more traditional variational basis representation (VBR) approach. To be concrete, the generic DVR proposed by Colbert and Miller has been used here.[23b] In particular, to get rid of the first derivative term of the radial part of the Hamiltonian, a new operational wave function φ has been defined as $r^{1/2}\Psi$.[23d]

Once the grid-point matrix representation of the Hamiltonian in (eq 1) has been built up, the energy levels and wave functions are obtained through diagonalization of this matrix. To be precise, the nuclear motion wave function is obtained as a linear combination of associated basis functions. Within the DVR we have used, the wave function φ_i associated with the eigenvector Ψ_i is expressed as

$$\varphi_i = \sum_{j=1}^{N_{\mathrm{p}}} c_{ij}\,\phi_j \quad (4)$$

where N_{p} is the total number of points in the grid. In our concrete three-dimensional case, ϕ_j has the following form:

$$\phi_j(r,R,\theta) = \left[\frac{\sin\left(\dfrac{\pi(r - r_k)}{\Delta r}\right)}{\pi(r - r_k)}\right] \times \left[\frac{\sin\left(\dfrac{\pi(R - R_l)}{\Delta R}\right)}{\pi(R - R_l)}\right] \times \left[\frac{1}{2\pi}\,\frac{\sin((\theta - \theta_m) \times (N + {}^{1}/_{2}))}{\sin\left(\dfrac{\theta - \theta_m}{2}\right)}\right] \quad (5)$$

where r_k, R_l, and θ_m are the coordinates of the point of the grid associated with basis function ϕ_j, and Δr and ΔR are the spacings in the r and R directions of the grid. N is related to the total number of points spawned in the angular coordinate, N^{θ}, by

$$N^{\theta} = 2N + 1 \quad (6)$$

The wave function is not necessarily normalized because the basis set given in eq 5 is a nonnormalized orthogonal basis set. Hence the wave function should be normalized prior to any further calculation involving it.

III. Results and Discussion

In this section we present first the results that are derived from pure electronic structure calculations, such as localization of stationary points and characterization of the potential energy barriers. Later we will present the results obtained through quantum nuclei motion calculations.

A. Electronic Structure Results. The first task to fulfill has been the localization of the minimum of the PES corresponding to the elongated dihydrogen structure of complex *trans*-$[\mathrm{Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2}]^+$. Along with this, the transition state structure corresponding to the rotational motion of the dihydrogen ligand has also been sought. Both structures are depicted in Figures 1 and 2, and a selected set of geometrical parameters of these structures is shown in Table 1, along with the corresponding parameters as determined by means of neutron diffraction studies for complex *trans*-$[\mathrm{Os(H\cdots H)Cl(dppe)_2}]^+$.[4b]

As can be seen in Table 1, there is good agreement between the structure of the minimum we have found and the geometry

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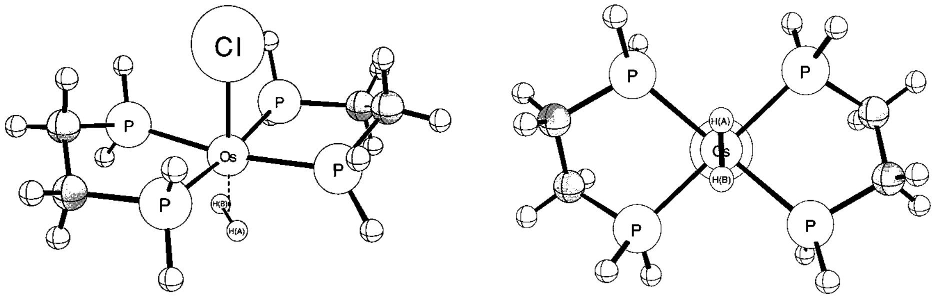

Figure 1. Minimum energy structure of complex *trans*-[Os(H···H)Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$]$^+$ (**1**) For the sake of clarity the structure is shown from two different perspectives.

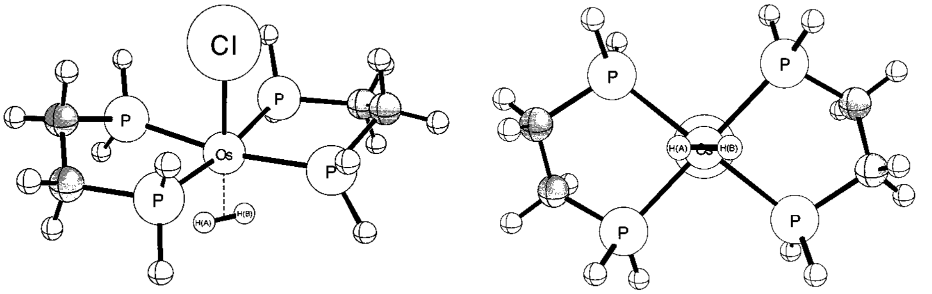

Figure 2. Transition state structure of the rotational motion of the dihydrogen unit in complex *trans*-[Os(H···H)Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$]$^+$ (**2**) For the sake of clarity the structure is shown from two different perspectives.

Table 1. Geometrical Parameters for Complex *trans*-[Os(H···H)Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$]$^+$ (Distances are in Å and angles in deg)

	neutron diffraction data[a]	minimum (**1**)	librational transition state structure (**2**)
Os−X(H$_2$)[b]	not given[c]	1.567	1.625
H−H	1.22(3)[d]	1.071	0.950
Os−H[d]	1.58	1.656	1.693
Os−P[e]	2.38	2.387	2.383
Os−Cl	2.44(1)	2.498	2.486
∠Cl−Os−P[e]	89.6	84.8	84.7
∠P−Os−P[e] (bite angles)	80.0	82.3	83.5
∠P−Os−P[e] (outer angles)	100.0	96.8	95.5
∠P−Os−P[e] (between opposite phosphorus atoms)	178.4	169.6	169.4

[a] Data for complex *trans*-[Os(H···H)Cl(dppe)$_2$]$^+$ from ref 4b. [b] X(H$_2$) stands for the point halfway between both hydrogen atoms in the H$_2$ unit. [c] Even though this distance could be calculated from the data in this table, only the correction for the H−H distance is known and not the correction for the Os−H ones, which would lead to an erroneous value. [d] This value has been corrected to take into account the librational motion of the H$_2$ unit. [e] Averaged values.

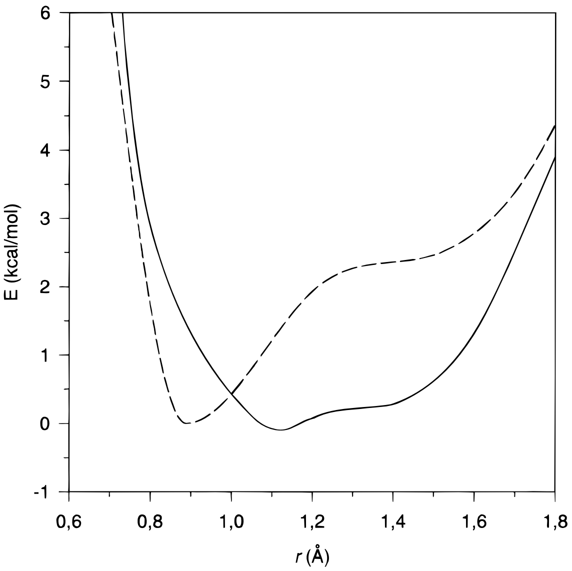

Figure 3. Energy profiles corresponding to the stretching of the H−H bond: solid line, complex *trans*-[Os(H···H)Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$]$^+$; dashed line, complex [Ru(H···H)(C$_5$H$_5$)(H$_2$PCH$_2$PH$_2$)]$^+$ (data from ref 8).

reported from experiment, at least referring to the parts of the complex other than the dihydrogen ligand. It is worth remembering that the actual complex has bulky groups in the chelating ligands, which could somewhat affect the geometry of the complex. The dihydrogen ligand in the minimum is staggered with respect to the linear P−Os−P axes, bisecting the P−Os−P angles of about 95° instead of the bite angles of the ligand, of about 80°. This same orientation was found by Maltby et al. in the neutron diffraction study of the complex.[4b] Also in agreement with experiment is the fact that all four phosphorus atoms are almost in the same plane. However, as happened in our previous study of the complex [Ru(H···H)(C$_5$H$_5$)(H$_2$PCH$_2$PH$_2$)]$^+$, the geometry of the dihydrogen ligand obtained through electronic structure calculations is in very poor agreement with the experimental data. In fact, electronic structure calculations predict that the minimum is an elongated dihydrogen complex with a H−H distance of 1.071 Å, whereas the structure reported experimentally has a quite long H−H distance of 1.22(3) Å.

To verify that the "correct" minimum has been found, the next step has been to construct the relaxed potential energy profile corresponding to the lengthening of the H−H bond in complex *trans*-[Os(H···H)Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$]$^+$, in which the whole range of H−H distances has been considered. At each point, the geometry of the complex has been optimized except for the H−H distance. This profile has been constructed at the same computational level than the localization of the minimum and the rotational transition state structure. The potential energy profile obtained in this way is depicted in Figure 3. For the sake of comparison, the corresponding potential energy profile for complex $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$, taken from ref 8, has also been plotted in Figure 3.

The monodimensional potential energy profile for the H−H stretch, displayed in Figure 3, is extremely flat. In contrast with what was found in the case of the ruthenium complex, in this case the degree of anharmonicity is even more important. Concretely, according to this graph, the stretch of this bond can go from the minimum to a distance of approximately 0.85 Å, or from the minimum to a distance of about 1.60 Å with a cost of merely 1 kcal/mol. As a side note, it is certainly shocking to realize that a bond so strong as the H−H one can be weakened in such a way as to be lengthened by 0.8 Å without a significant rise in energy. The possibility that elongated dihydrogen complexes could be described as shallow minima in the potential energy surface had already been suggested by some authors.[4] The common feature encountered in the potential energy profiles corresponding to the H−H stretch in complexes *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$ and $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$, that is, the high degree of anharmonicity of both profiles, seems to indicate that such profiles could be the norm rather than the exception of the so-called elongated dihydrogen complexes.

On a different subject, the rotational potential energy barrier of the dihydrogen unit has been found to be 2.03 kcal/mol. This value is considerably smaller than the value of the same barrier we determined for complex $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$ (4.23 kcal/mol). The difference in magnitude of both rotational barriers is in agreement with the experimental behavior displayed by both complexes. Hence, the low value of the rotational barrier in the osmium complex is consistent with the complex being between the fast and slow spinning limits, whereas the ruthenium complex, having a higher rotational barrier, is in fact a slow spinning dihydrogen complex. The value of the barrier is comparable to the values found by inelastic neutron scattering (INS) in complexes $Mo(CO)(\eta^2\text{-}H_2)(dppe)_2$,[24a] $[FeH(\eta^2\text{-}H_2)(dppe)_2]^+$,[24b] and $Tp^{Me2}Rh(\eta^2\text{-}H_2)H_2$,[24c] which was in all cases below 2.5 kcal/mol. As a final note, the energy of dissociation of H_2 from the rest of the complex has been calculated to be 34.9 kcal/mol. This value is higher than the corresponding value for the ruthenium complex (22.7 kcal/mol),[8] indicating that from the purely electronic point of view the H_2 unit is more strongly bound to the osmium complex, and that the H−H bond is weaker in this complex than in the ruthenium one.

B. Nuclear Motion Results. The main result of the preceding part has been the realization of the fact that the H−H stretch is even more anharmonic than it was in the case of the ruthenium complex we studied before.[4d] In the case of the ruthenium complex, with an anharmonicity much smaller, nuclear motion calculations were the key to understanding the complex's properties. The same is likely to happen here, even though applying the same procedure will meet with novel difficulties in this case. In this section we will evaluate the vibrational energy levels and wave functions of the $Os-H_2$ unit in complex *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$.

The first mandatory step is the evaluation of $U(\boldsymbol{R})$, the potential energy hypersurface of the complex. As stated in the Calculational Details section, the evaluation of the whole $U(\boldsymbol{R})$ is unfeasible. Accordingly, only a reduced PES will be calculated here. Given that we are interested in the dynamics of the $Os-H_2$ unit of the complex, we need at the very least to include two geometrical parameters, which are the H−H and the $Os-H_2$ stretches (henceforth, r and R, respectively). However, in this case, conversely to what happened in the ruthenium complex, the degree of freedom corresponding to the librational motion of the H_2 unit (θ) has a low potential energy barrier (2.03 kcal/mol), so that it must be taken into account in an explicit way.

What should be done now is to carry out a series of electronic structure calculations on a set of molecular geometries covering all the available configurations of these geometrical parameters (r,R,θ). However, if a total of N points are needed in order to correctly describe one of these degrees of freedom, building the reduced three-dimensional version of U implies the calculation of N^3 points, each corresponding to an electronic structure calculation. It is easy to see that this option would prove to be exceedingly costly in computational terms. To reduce the cost of the computation, the effects of the librational degree of freedom (θ) will be introduced in an approximate way. Given that the librational barrier is very small, the changes that it can undergo as a result of the lengthening of the H−H distance can be very important in relative terms. Due to this fact, and given that we are interested in measuring both the value of the H−H distance and its dependence with temperature, our approximate potential energy surface must be flexible enough as to give different librational potential energy barriers for different H−H distances. Due to this, a maybe crude but appropriate description of this approximate potential energy surface could be

$$V(r,R,\theta) = V_{\text{stretch}}(r,R) + V_{\text{libration}}(\theta;r) \qquad (7)$$

where V_{stretch} corresponds to the potential energy of the complex when the phase of the librational motion is the same as in the minimum (Figure 1), and $V_{\text{libration}}$ describes the potential energy profile along the librational motion of the dihydrogen ligand for a given set of H−H (r) and $Os-H_2$ (R) distances.

To evaluate V_{stretch}, a series of electronic structure calculations has been performed by fixing the phase of the librational motion to be the same as in the minimum, and then allowing the complex to relax its structure for each given pair of H−H and $Os-H_2$ distances. The range of H−H distances covered from 0.6 to 2.2 Å, while the $Os-H_2$ distance went from 1.0 to 2.2 Å. A total of 8 grid points were allocated in the r direction, while 7 where allocated in the R one, for a grand total of 56 optimizations. The resulting mesh of points was fitted into a two-dimensional cubic splines functional form, which is a smooth and continuous function.[25] A contour plot of V_{stretch} is shown in Figure 4. This plot bears some similarities with the corresponding one for complex $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$.[8] Concretely, it can be seen that the extension of the potential energy valley is similar. Also similar is the fact that there is extensive mixing of the H−H and $Os-H_2$ stretchings, which can be visualized in the oblique shape of the potential energy valley in Figure 4. The fact that the H−H stretch cannot be viewed as an isolated normal mode in transition metal dihydrogen complexes has been pointed out in a recent work by Bender et al.[26] This potential energy valley presents an exit at $r \approx 0.80$ Å, which leads to the complex emitting H_2. The asymptotic value of this exit has been determined, as explained in Section III.A, to be of 34.9 kcal/mol.

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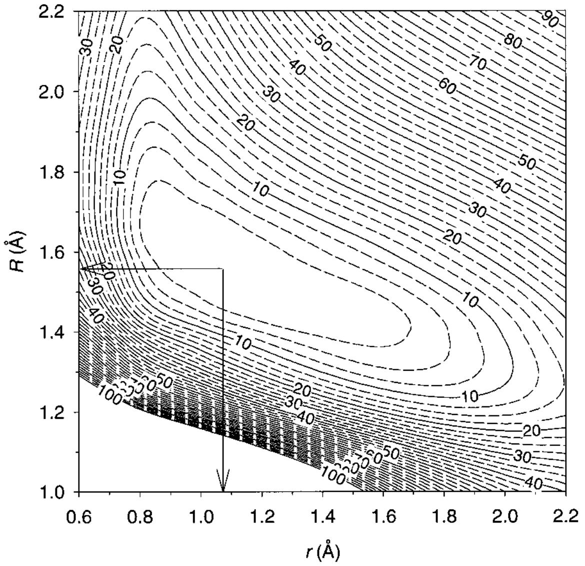

Figure 4. Contour plot of $V_{stretch}(r,R)$ for complex *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$. Potential energy contours appear every 2.5 kcal/mol. The arrows indicate the position of the minimum energy structure ($r = 1.071$ Å, $R = 1.567$ Å)

As for $V_{libration}$, what has been done is, essentially, to determine the dependence of the potential energy barrier of the librational motion of the H_2 unit on the elongation of the H−H bond (r). To this end, a possibility is to write $V_{libration}$ as

$$V_{libration}(\theta;r) = W(\theta)V^{\ddagger}(r) \qquad (8)$$

where $W(\theta)$ is a cutoff function that takes on the value of unity when the value of the librational (θ) reaches the librational transition state structure, and the value of zero when the phase of such motion corresponds to that of the minimum. If we assign $\theta = 0$ to a librational phase such as that depicted in Figure 1 (that is, the minimum), then it is easy to see that there is a librational transition state at $\theta = \pi/2$ (which corresponds to Figure 2). Due to symmetry reasons, a new identical minimum appears when $\theta = \pi$, and a further transition state structure exists when $\theta = 3\pi/2$. We have chosen the following simple functional form for function $W(\theta)$, which fulfills these simple requirements:

$$W(\theta) = \sin^2 \theta \qquad (9)$$

Parenthetically, we note that a similar functional form has been previously used for $V_{libration}$ by several authors when studying the librational dynamics of the H_2 unit in dihydrogen complexes.[24c,27] Finally, to determine the dependence of the librational potential energy barrier on the H−H stretch, $V^{\ddagger}(r)$, we have opted for determining the energy barriers along the minimum energy path that leads from the minimum (an elongated dihydrogen) to the area of the PES corresponding to the dihydride, and also from the minimum to the area in which the H_2 unit dissociates from the complex. This has been done by optimizing the structure of the complex for different values of r, and then determining the librational potential energy barrier for each of them, keeping fixed the geometry of the Os−H_2 unit but making the phase of the librational motion to be $\pi/2$, and allowing the rest of the geometrical parameters of the complex to vary in the optimization. The corresponding energy difference is directly $V^{\ddagger}$. The resulting values of $V^{\ddagger}$ were fitted into a simple cubic splines functional form to ease the ensuing calculations.[28] A graphical representation of the function $V^{\ddagger}(r)$ is depicted in Figure 5.

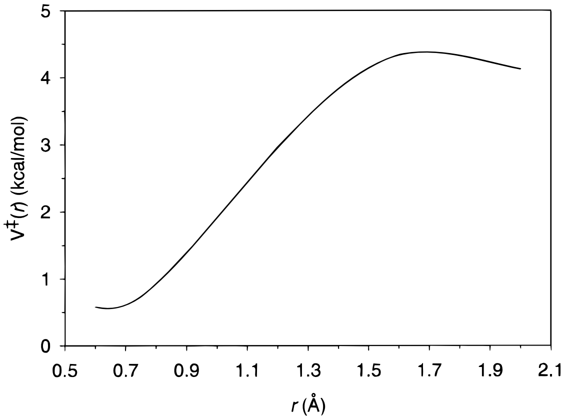

Figure 5. Dependence of the librational potential energy barrier on the elongation of the H−H bond.

As expected, increasing the H−H distance makes it more difficult to rotate the dihydrogen ligand (which at the rightmost part of the plot is more accurately described as a dihydride). The potential energy barrier for rotating the dihydrogen ligand reaches values of almost 4.5 kcal/mol when the H−H distance is of about 1.6 Å. It is worth mentioning that the librational potential energy barrier we determined in subsection A is not strictly a point in this plot. The reason for this is that, in this plot, each point corresponds to the difference in potential energy between a structure in which $\theta = 0$ and another in which $\theta = \pi/2$, in which all the geometrical parameters of the complex barring r and R have been allowed to relax. On the other hand, in the case of the librational potential energy barrier we determined in Section III.A (2.03 kcal/mol), *all* the parameters, including r and R, have been allowed to vary when optimizing.

It is now possible to perform the three-dimensional quantum nuclear motion calculations. Prior to that, it is worth remembering some things. First, the lowest value along the borders of the plot of $V_{stretch}$ in Figure 4 is of about 16 kcal/mol, which means that only energy levels below this value can be reliably determined. However, the approximations involved in eqs 7−9 when introducing the librational degree of freedom in an explicit way will affect the results of these calculations, so that the quantitative validity of these results may be affected. The concrete details of the nuclear motion calculations are as follows: the number of points spawned in the r, R, and θ axes were, respectively, 22, 22, and 19. This would have led to a total of 9196 points, and hence, to a Hamiltonian matrix 9196 × 9196 in size, far too big to work with. Accordingly, we have truncated the grid by discarding the grid points whose potential energy exceeds a given cutoff value, because the value of the wave function at these points will be nonnegligible only in highly excited states similar in energy to the point's own potential energy. This strategy has been used previously with success.[23b] By imposing the cutoff value to be the value of the lowest energy along the perimeter of $V_{stretch}$ in Figure 4, the number of points was reduced to 1313, far less than before and substantially easier to work with. It was checked that an increase in the number of points did not in a significant way alter the position of the energy levels. A summary of the results of this calculation is shown in Table 2.

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Table 2. Vibrational Energy Levels for the Os−H_2 Unit in Complex *trans*-[Os(H···H)Cl($H_2PCH_2CH_2PH_2$)$_2$]$^+$

energy level	E (kcal/mol)[a]	$\langle r\rangle$ (Å)	$\langle R\rangle$ (Å)	energy level	E (kcal/mol)[a]	$\langle r\rangle$ (Å)	$\langle R\rangle$ (Å)
0	3.97[b]	1.234	1.529	6	5.93[c]	1.326	1.510
1	3.97[b]	1.235	1.529	7	5.93[c]	1.208	1.542
2	4.79	1.231	1.531	8	5.94	1.328	1.509
3	4.80	1.233	1.530	9	6.08	1.256	1.525
4	5.43	1.235	1.532	10	6.33	1.215	1.540
5	5.46	1.247	1.528				

[a] Energies are relative to the minimum in the PES. [b,c] These levels appear as degenerate only due to the fact that only two decimal figures are shown for energies.

Table 3. Ground State Expectation Values for H−H (r) and M−H_2 (R) Distances

	complex					
	trans-[Os(H···H)Cl($H_2PCH_2CH_2PH_2$)$_2$]$^+$			[Ru(H···H)(C_5H_5)($H_2PCH_2PH_2$)]$^{+\,a}$		
isotopic composition	E_0 (kcal/mol)	$\langle r\rangle$ (Å)	$\langle R\rangle$ (Å)	E_0 (kcal/mol)	$\langle r\rangle$ (Å)	$\langle R\rangle$ (Å)
H−H	3.97	1.234	1.529	4.58	1.024	1.605
H−D	3.25	1.224	1.528	3.92	0.994	1.615
D−D	2.66	1.206	1.531	3.28	0.958	1.631

[a] Taken from ref 8.

In Table 2 only the first few vibrational energy levels are shown. In the second column of Table 2, the energies of the vibrational energy levels are shown, relative to the minimum of the PES. It can be seen that the Os−H_2 unit contributes substantially to the zero-point vibrational energy (ZPE) of the complex (3.97 kcal/mol). Once the nuclear eigenfunction Ψ_i for a given vibrational level i is known, it is straightforward to determine the expectation value for a given observable a by means of

$$<a> = \frac{\langle \Psi_i|\hat{a}|\Psi_i\rangle}{\langle \Psi_i|\Psi_i\rangle} \tag{10}$$

where $\hat{a}$ is the quantum mechanical operator associated with observable a. If a is a geometrical parameter, then $\hat{a}$ is directly the corresponding variable. In this way the expectation values for r and R have been calculated for the first vibrational levels, and are shown also in columns three and four of Table 2. In all cases, the expectation value of the librational parameter, $\langle\theta\rangle$, is 0, that is, the H_2 unit is aligned exactly as it is in the minimum.

Yet another time, the most striking result comes from the expectation value of the H−H dihydrogen distance (r) for the ground vibrational state of complex *trans*-[Os(H···H)Cl($H_2PCH_2CH_2PH_2$)$_2$]$^+$. It can be seen in Table 2 that in the vibrational ground state we predict a value of 1.234 Å, in amazingly good agreement with the experimental results (1.22(3) Å).[4b] However, this agreement must not be given more significance than it deserves. It is time to remember, for instance, that the PES used to reach this value has an inherent approximation in it, contained in eq 7, which can affect the numerical accuracy of the final results. What is really important and significant is that, similar to what happened with the ruthenium complex [Ru(H···H)(C_5H_5)($H_2PCH_2PH_2$)]$^+$,[8] nuclear wave function calculations predict a substantial deviation of the expectation value of r from the position of the minimum in the PES, and that these calculations manage to describe this deviation almost quantitatively in both cases.

Given that vibrational energy levels are dependent on the mass of the atoms of the complex, it is predicted that isotopically substituting the dihydrogen ligand in the complex will alter the Os−H_2 vibrational levels somewhat, and hence, this will cause changes in the expectation values of the geometrical parameters r and R as long as the nuclear wave function is modified accordingly. The vibrational ground levels for the Os−H_2 unit of the complex have been calculated for a few isotopic variants of the complex, and are summarized in Table 3 along with the expectation values of r and R in each case. For the sake of comparison the previous results corresponding to the ruthenium complex are also shown in Table 3.

As could be expected, dependence of the geometrical parameters on isotopic composition of the Os−H_2 unit is predicted, in such a way that the H−H distance is shortened when heavier isotopes are used. However, compared to the magnitude of the effect in the ruthenium complex it can be seen that the corresponding change is sensibly smaller. The explanation of this could be that in the case of the ruthenium complex and due to the particular shape of its PES (best envisaged by looking at the monodimensional H−H stretch in Figure 3), a decrease in the ZPE leads to an important localization of the nuclear wave function in the neighborhood of the PES minima. Conversely, in the case of the osmium complex the almost totally flat potential energy profile for the H−H stretch in the zone where nuclear motion energy levels have been calculated indicates that lowering the value of the ZPE should not, and indeed does not, localize the nuclear wave function to the same extent. The consequence of this is that in the case of the osmium complex, there is much less sensitivity of the H−H distance with isotopic substitution, which changes only by 0.028 Å when going from the H−H isotopomer to the D−D one. In contrast, in the ruthenium complex this same isotopic change provokes a decrease of 0.07 Å.

An interesting experimental datum that remains unexplained is the temperature dependence of the J(H,D) coupling constant in this complex. Experimentally, the value of the J(H,D) coupling constant has been observed to vary from 13.6 Hz at 253 K to 14.2 Hz at 308 K when the solvent is CD_2Cl_2, that is, an overall increase of 0.6 Hz in an interval of temperature of 55 K.[4b] According to the empirical correlations that have been determined, there seems to be a linear relationship between H−H distance and the value of the J(H,D) coupling constant.[4,10,11] The complex under study displays increasing J(H,D) coupling constant values with increasing temperature, which according to these empirical correlations seems to indicate that the H−H distance becomes shorter when temperature increases. In other words, it seems that vibrationally excited states of the Os−H_2 unit ought to have shorter $\langle r\rangle$ values. This last statement can readily be checked by examining Table 2. In fact, the first feature of the set of nuclear motion energy levels that draws

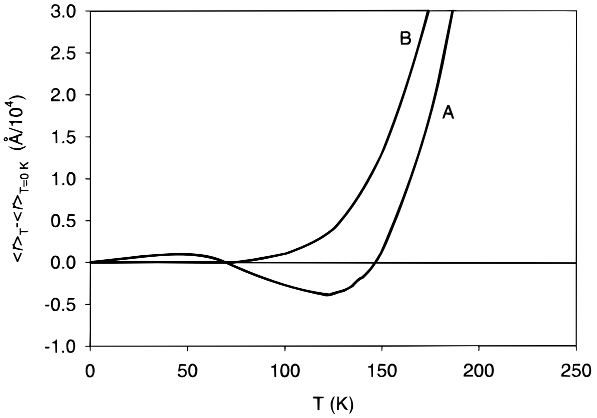

Figure 6. Temperature dependence of the thermal average H−H distance in complex *trans*-[Os(H•••H)Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$]$^+$. The *y*-axis magnitude depicted corresponds to the deviation from the value of the H−H distance at $T = 0$ K, which is also the horizontal line. Line A shows results derived from using a three-dimensional version of the PES ($V(r,R,\theta)$); B, results derived from a bidimensional version of the PES ($V(r,R)$).

attention is the fact that there are many energy levels densely packed. This means that, even at low temperatures, many vibrational levels are likely to have nonnegligible populations and will, hence, contribute substantially to the averaged thermal value of the H−H distance. Moreover, it can be seen that there is not a monotonic trend relating the average H−H distance in a vibrational state with the energy of the state, which is to say that an excited vibrational state not always has a longer expectation H−H distance than the vibrational state immediately below. This could mean that on increasing temperature, these excited vibrational states with short expectation H−H distances could become populated enough as to provoke a global decrease of the mean thermal H−H distance. To check this fact, we have calculated mean thermal H−H distances for the H$_2$ isotopomer of the osmium complex under study for a given range of temperatures by assuming a Boltzmann equilibrium distribution considering only vibrational states within 5 kcal/mol of the vibrational ground state, so that the population of the most excited states considered was almost zero. The results are graphically displayed in Figure 6.

First of all, it is worth highlighting the fact that there is an interval of temperatures (~50−130 K) for which we predict that the mean thermal H−H distances will actually *decrease* with increasing temperature (hence, J(H,D) values will increase in this interval), in this way *qualitatively* reproducing the experimentally observed behavior. This is due to the increasing contribution to the mean thermal H−H distance coming from excited vibrational states with shorter H−H distances. However, we fail to reproduce *quantitatively* the interval of temperatures in which the decrease of H−H distances takes place. In fact, experimentally the only behavior observed, to our knowledge, has been the decrease of H−H distances along with increasing temperature for the range of temperatures between 253 and 308 K. In addition to that, the magnitude of the decrease predicted by our calculations is smaller than it ought to be. We think that this lack of ability to reproduce both the experimental behavior in a broader interval of temperatures and the magnitude of the shortening of the H−H distance has its roots in the approximations used to construct the potential energy surface. Be it as it may, we think that it is highly significant that by introducing the librational motion explicitly in this case, an interval of actual H−H distance decrease with increasing temperature is predicted. This fact alone validates the three-dimensional potential energy surface used in this paper and described in eqs 7 and 8, which even though it is approximate, it is good enough as to explain the experimentally reported behavior. The experimentally observed effect is subtle enough so that the use of approximations in the theoretical model makes it unable to reproduce the experimental evidence in a quantitative way.

Table 4. Vibrational Energy Levels for the Os−H$_2$ Unit of Complex *trans*-[Os(H$_2$)Cl(H$_2$PCH$_2$CH$_2$PH$_2$)$_2$]$^+$, Obtained When Disregarding the Librational Degree of Freedom θ

energy level	E (kcal/mol)[a]	$\langle r \rangle$ (Å)	$\langle R \rangle$ (Å)
0	3.52	1.202	1.536
1	5.36	1.264	1.531
2	7.54	1.281	1.535
3	9.42	1.256	1.541
4	10.08	1.282	1.549

[a] Energies are given relative to the minimum in the PES.

The main difference between the treatment of the metal−H$_2$ unit that has been used here and the one used in the case of the ruthenium complex is the explicit consideration of the librational motion of the dihydrogen unit of the complex, because in this case the librational motion has a potential energy barrier much lower than in the case of the ruthenium complex. One could wonder what would happen in this case if a similar approach were used to treat the motion of nuclei in the osmium complex, that is, what would happen if the librational degree of freedom were not included explicitly. To do this, we have performed again the quantum nuclear motion calculations, but this time only considering the H−H and Os−H$_2$ stretches as variables for U. In other words, the reduced PES for the motion of the dihydrogen unit is now precisely $V_{\text{stretch}}(r,R)$. As was mentioned previously in Section II, the corresponding two-dimensional (2D) calculation is in all ways analogous to the one we presented in our previous work on the complex [Ru(H•••H)(C$_5$Me$_5$)(dppm)]$^+$.[8] The corresponding vibrational energy levels obtained in this 2D calculation are shown in Table 4, along with the expectation values for the H−H and Os−H$_2$ distances.

Some aspects are worth commenting. It can be seen that the ground vibrational state is found only 0.45 kcal/mol below its position in the complete 3D calculation. The increase in the value of the zero-point energy level in the 3D calculation is due to the introduction of the librational degree of freedom θ, and should have been zero (that is, both energies should match) if we had considered the dihydrogen unit to be a rigid rotor. Apart from that, the vibrational energy levels are sparser in the 2D calculation than in the 3D one, also due to the introduction of the librational degree of freedom in the latter case.

It can be seen that even with a 2D calculation the expectation value for the H−H distance (1.202 Å) is in very good agreement with the experimentally reported value (1.22(3) Å), so that it seems that after all maybe a complex 3D calculation was not necessary. However, a cursory inspection of the expectation values for the H−H distance for each energy level will reveal that contrary to what happened in the 3D case, now there is a clear trend toward lengthening the H−H distance in the higher vibrational states. Only one energy level has an expectation value for the H−H distance shorter than the one of the energy level immediately below (level 4), and even in this case the expectation value for the H−H distance is sensibly longer than the one of the ground vibrational energy level. As a consequence, a monotonic increase of averaged thermal H−H distances with temperature would be expected if a mere two-dimensional quantum nuclear motion calculation had been performed. In effect, the predicted temperature dependence of the H−H distance when the librational degree of freedom is not considered is displayed in Figure 6, along with the predicted temperature dependence of the same magnitude when the librational degree of freedom is taken into account. As can be seen, there is a clear difference between them, for only when the librational degree of freedom is considered explicitly is an actual decrease of the H−H distance predicted.

IV. Conclusions

In this paper we have studied the complex *trans*-$[Os(H\cdots H)Cl(H_2PCH_2CH_2PH_2)_2]^+$, taken as a realistic theoretical model of *trans*-$[Os(H\cdots H)Cl(dppe)_2]^+$. This complex has been classified as being between the fast and slow spinning regimes, with regard to the rotational dynamics of the H_2 unit of the complex.[4b] The most significant conclusions of this work are the following ones:

Electronic structure analysis has proved to be unable to explain the geometry observed by means of neutron diffraction of the $Os-H_2$ unit of the complex, even though the rest of the complex is described properly. Concretely, electronic structure calculations predict a much shorter H−H distance, as happened with our previous study of complex $[Ru(H\cdots H)(C_5H_5)(H_2PCH_2PH_2)]^+$.[8] However, a quantum study of the motion of the light nuclei predicts almost quantitatively the right geometry for the $Os-H_2$ unit of the complex. Given that this is the second elongated dihydrogen complex that has been satisfactorily explained in this way, it seems likely that this feature is common to the so-called elongated dihydrogen complexes.

Qualitative success has been achieved when trying to explain the experimentally reported temperature dependence of the ^1H NMR J(H,D) coupling constant, but only when taking into account explicitly the librational degree of freedom of the H_2 unit of the complex. It has been observed that the value of the librational potential energy barrier depends on the elongation of the H−H distance, becoming higher the longer the H−H distance becomes. The effects of this behavior are that the potential energy valley becomes wider in the areas of the PES in which the H−H distance is small, and narrower in these zones of the PES in which the H−H distance is longer. Accordingly, there could be (and actually, there are) certain low-energy vibrational states whose nuclear wave function is able to "spread" toward these wide potential energy valleys, which are found in short H−H distance zones of the PES, in this way leading to short expectation values for the H−H distances.

In conclusion, we think that our methodology is able to justify almost quantitatively the existence of the elongated dihydrogen complexes. As for the temperature dependence of the J(H,D) coupling constant, be it "normal" (ruthenium complex—ref 8) or "inverse" (osmium complex—this work), we believe that we have identified the physical causes behind the phenomenon, although no quantitative description is possible yet, due to the high cost of the computations involved if a more realistic model for the potential energy was to be devised.

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