



Dose type of phosphine affect rotational barrier of vinylidene in the complexes $\text{OsHCl}(\text{C}=\text{CH}_2)(\text{L})_2$ (L = phosphine)?

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9 Abstract

Density functional molecular orbital calculations at the BP86 level were performed to investigate rotational barrier of vinylidene ligand in the model complexes $\text{OsHCl}(\text{C}=\text{CH}_2)(\text{L})_2$ (L = PMe_3 , PH_3 , PF_3). Results of calculations indicate that the rotational barrier increases with the increasing π -accepting ability of phosphine. This result has been explained on the basis of the extent of π -interaction between metal and vinylidene ligand in the complexes.

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Chemistry of osmium- and ruthenium-carbon multiple bonds has experienced much progress in recent years. The vinylidene complexes are regarded to be important because of their potential as reactive intermediates in organic and organometallic synthesis as well as in catalytic processes [1]. In recent years, a lot of complexes by the general formula of $\text{MX}'\text{Cl}(\text{C}=\text{CHR})(\text{L})_2$ (M = Ru/Os ; X' = H , CHCMe_3 , Cl , etc.; R = Ph , SiMe_3 , etc.; L = phosphines) have been synthesized and characterized [2–6]. Theoretical studies on such complexes indicate that the π -accepting substituents in X' or R would reduce the rotational barrier in vinylidene [7]. In such case, by the help of NMR apparatus is seen no more two rotational isomers. A question can immediately be raised. Do π -accepting phosphines also reduce the rotational barrier of vinylidene? In this paper, we attempt to answer this question with the aid of pure density functional theory (DFT).

All the DFT (BP86) [8] calculations were performed with Gaussian-98 software package [9]. The effective core potentials (ECPs) of Hay and Wadt [10] with double- ζ valance basis sets (LanL2DZ) were used to describe Os, P, and Cl. The 6-31G basis set was used for all other atoms [11]. Polarization functions were also added for Cl ($\zeta_d = 0.514$), P ($\zeta_d = 0.340$), F ($\zeta_d = 0.8$), H (hydride; $\zeta_d = 1.1$) [12], and C (vinylidene; $\zeta_d = 1$). Natural bond orbital (NBO) analyses were performed using the NBO program [13] as implemented in Gaussian-98 program.

At first the structures of model complexes $\text{OsHCl}(\text{C}=\text{CH}_2)(\text{PX}_3)_2$ (X = CH_3 , H , and F) were fully optimized with pure DFT (BP86) method (see 1; GS-X). To investigate the effect of phosphine ligands on rotational barrier of vinylidene, we performed calculations through rotation of vinylidene by 180° about the Os–C axis (see 2; TS-X). The selected optimized geometries of these model complexes have been listed in Table 1. The calculated structural parameters for model complexes GS-H and TS-H at BP86 level are in good agreement with the results obtained from B3LYP level calculations [7,14].

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Table 1

The optimized selected structural data (Å, °) for the conformations GS-X and TS-X

	GS-X			TS-X		
	GS-CH ₃	GS-H	GS-F	TS-CH ₃	TS-H	TS-F
Os–C	1.823	1.835	1.857	1.824	1.837	1.856
Os–P	2.370	2.347	2.286	2.383	2.356	2.296
P–Os–P	176.2	178.3	174.5	165.2	165.3	166.1

Frequency calculations for all model complexes confirmed that conformations GS-X are indeed ground state, whereas conformations TS-X are transition state. The imaginary frequency of TS-X corresponds to the rotation of vinylidene ligand, which transforms TS-X → GS-X.

Energy differences between each pair of model complexes are shown in Table 2. In view of the results obtained from the calculations, one can observe that rotational barrier of vinylidene increases in the order of GS-F > GS-H > GS-CH₃. As it was reported earlier [15], the σ -donation properties of these phosphine ligands are ordered as PF₃ > P(Me)₃ > PH₃, while π -accepting abilities of them are ordered as following: PF₃ > PH₃ > P(Me)₃. In addition, as mentioned above, the molecular orbital calculations of similar complexes, OsX'Cl(C=CHR)(PH₃)₂, also indicate that rotational barrier increases by substitution of X' or R from having π -acceptor to σ -donor properties [7]. Since Os–X' and Os–PX₃ bonds are approximately perpendicular to each other, these results in fact complementary to our DFT studies, in which the rotational barrier of vinylidene by increasing π -accepting properties of phosphine ligands enhances.

Vinylidene ligand has a low-lying p orbital, which can be considered as a single face strong π -acceptor ligand. In most stable conformations (GS-X), LUMO of vinylidene ligand, i.e., Cl p_z orbital, interacts with Os d_{yz} orbital (Fig. 1(a)), while d_{xy} orbital from the metal center interacts with a low-lying empty hybrid orbital of phosphine [16] (a combination of a 3d orbital with a P–H σ^* orbital) (Fig. 1(b)). In this case, Os–vinylidene back-bonding interaction is maximized. In the transition state, hybrid orbital of phosphine as well as Cl p_x orbital of vinylidene ligand interact with d_{xy} orbital (Fig. 1(c)). As a result, one expects that the significant destabi-

lization of conformations TS-X compared with GS-X, can be explained by sharing the same Os d orbital for metal(d)-to-ligand backbonding between vinylidene and phosphine ligand.

In conformations GS-X, the observed significant structural changes are in the Os–P and Os–C bond distances (see Table 1). The Os–C bond distances decrease drastically, by a maximum of 0.34 Å, from X = F to H and then to CH₃, while the changes of Os–P bond distances are in the opposite direction. Taking into account electronic features of corresponding phosphines, it seems that central metal along with PMe₃ ligands have much more ability for π -backdonation to vinylidene's Cl p orbital. This strengthens the Os–C and simultaneously weakens the Os–P bonding along the series of X in conformations GS-X. Examining the results obtained from the calculations, it is evident that Os–P bond distance is lengthened and, at the same time, P–Os–P bond angle is decreased from conformations GS-X to their corresponding TS-X (see Table 1). The bending of P–Os–P is expected to enhance the d_{xy}-p backbonding interaction between the metal and vinylidene moieties, which is resulted in a decrease in Os–P π -interaction.

The natural orbital populations of Cl p_z orbital in the most stable conformations and Cl p_x orbital in the transition states are suitable criteria for determining the extent of Os–Cl π -interaction, since those are mainly involved in the π -backdonation interaction (see Fig. 1). The natural orbital populations of both cases are listed in Table 3. The natural orbital populations of Cl p_z orbitals are ordered as GS-CH₃ > GS-H > GS-F, which clearly show that the strength of Os–Cl π -interaction becomes stronger in the same order. The natural orbital population analysis of p_x also indicates a similar trend. In all conformations, natural orbital populations of Cl p_z orbitals are higher than those of Cl p_x. These population changes can be explained on the basis of the fact that complexes in the GS-X experience more favorably Os–Cl π -bonding interaction, since in TS-X, π -acceptor characteristic of phosphine ligands competes with the metal-to-vinylidene backdonation. In addition, the differences of natural orbital populations of p_z in the conformations GS-X and those of p_x in their corresponding TS-X increase in the order of PF₃ > PH₃ > P(Me)₃, which is consistent with our DFT calculations that rotational barrier of vinylidene becomes higher in the same order.

Table 2

Rotational barriers (kcal/mol) of vinylidene ligand without zero-point energy corrections (ΔE), with zero-point energy corrections ($\Delta E + \text{ZPE}$), and free energies (ΔG) in OsHCl(C=CH₂)(L)₂ model complexes

Rotational barrier (kcal/mol)	GS-CH ₃ → TS-CH ₃	GS-H → TS-H	GS-F → TS-F
ΔE	6.6	8.1	9.7
$\Delta E + \text{ZPE}$	6.1	7.6	9.0
ΔG	5.7	6.8	9.0

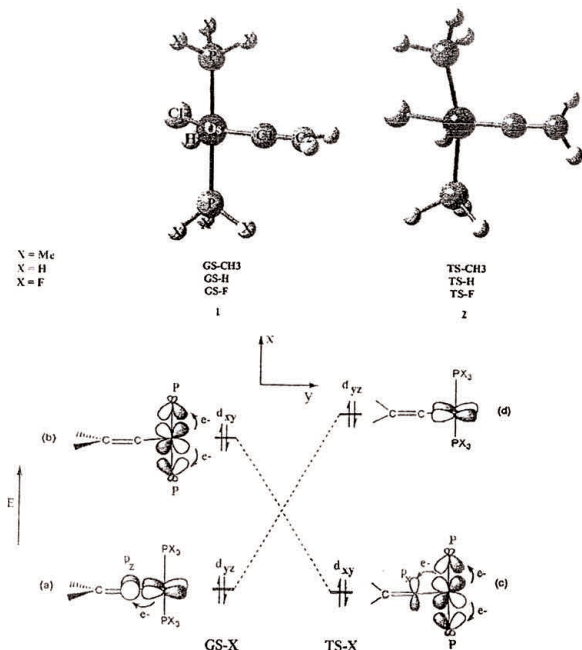


Fig. 1. The correlation diagram between d_{xy} and d_{yz} orbitals within conformations GS-X and TS-X

Table 3

The natural orbital populations of Cl p_x orbital in GS-X and Cl p_x orbital in TS-X as well as difference of natural orbital population of p_x in the conformations GS-X and that of p_x in their corresponding TS-X

	GS-CH3	TS-CH3	GS-H	TS-H	GS-F	TS-F
ϵ	0.8122	–	0.8003	–	0.7532	–
p_x	–	0.6701	–	0.6382	–	0.5697
$p_x - p_x$	0.1421	0.1421	0.1621	0.1621	0.1836	0.1836

The results are understood based on the fact that a strong π -acceptor phosphine ligand, such as PF_3 , can stabilize the Os d orbital, particularly d_{xy} , reducing effective

bonding interaction with Cl p orbital. In other words, PF_3 groups compared with the other phosphines are able to more significantly stabilize d_{xy} orbital in the

143
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145

Table 4

The energy difference (a.u.) between the d_{xy} and d_{yz} ($|d_{xy} - d_{yz}|$) in the model complexes as well as difference of $|d_{xy} - d_{yz}|$ energy gap (a.u.) ($\Delta\Delta E$) between GS-X and its corresponding TS-X

	GS-CH ₃	TS-CH ₃	GS-H	TS-H	GS-F	TS-F
$ d_{xy} - d_{yz} $	0.05686	0.06833	0.05211	0.06793	0.04776	0.07713
$\Delta\Delta E$	0.01147	0.01147	0.01582	0.01582	0.02937	0.02937

transition states, and consequently, reduce Os–Cl interaction. Therefore, the complex containing more π -acceptor phosphine ligands can relatively destabilize transition state compared with its corresponding ground state. This effect is also supported from difference of $|d_{xy} - d_{yz}|$ energy gap ($\Delta\Delta E$) between GS-X and its corresponding TS-X in which $\Delta\Delta E$ is ordered as $\text{PF}_3 > \text{PH}_3 > \text{P}(\text{Me})_3$ (see Table 4). Taking trends obtained from the calculations into consideration, one expects that the bigger barrier for the complex with PF_3 can be related to relative destabilization of the transition state, resulting from sharing d_{xy} orbital between the hybrid orbital of PF_3 and the C1 p_x orbital of vinylidene. It also seems that π -accepting substituents in X' or R relatively cause destabilization of the most stable conformations; therefore, they decrease the rotational barrier of vinylidene ligand.

The present calculation results indicate that for a given structure, when the Os– PX_3 π -backbonding interactions are stabilizing, the Os–X and Os–C π -backbonding interactions would be destabilizing and vice versa. Thus, different stabilizing effects are observed for PX_3 , R, and X ligands.

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