Theoretical Studies of Rotational Barriers of Vinylidene Ligands in the Five-Coordinate Complexes M(X)Cl(=C=CHR)L_2 (M = Os, Ru; L = Phosphine)

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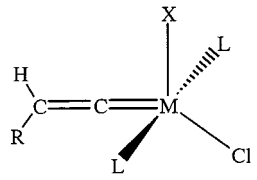
Rotational barriers of vinylidene ligands in the five-coordinate complexes M(X)Cl(=C=CHR)L_2 (M = Os, Ru; L = phosphine) have been investigated by density functional theory calculations at the level of B3LYP. The effects of ligand X, transition metal M, and substituent R on the barriers have been examined. The results show that the rotational barriers increase with X from having π-acceptor, σ-donor to having π-donor properties. Ligands (X) with π-acceptor properties stabilize the transition state structures through interactions with the d orbital used for metal−vinylidene π bonding in the most stable conformations and, therefore, give smaller rotational barriers. Studies of the influence of different substituents R show that the rotational barriers also increase with the electron donation abilities of R. The rotational barriers for Os complexes are generally higher in comparison to those of the Ru analogues. This result is related to the stronger osmium−ligand interactions because of the more diffuse d orbitals of the heavier metal.

Introduction

Transition-metal vinylidene complexes have attracted much attention in the past decade because they are considered as important intermediates in many stoichiometric and catalytic transformations of organic molecules.[1,2] In particular, vinylidene complexes can promote C−R bond formation and olefin metathesis reactions.[3,4] Among the studied vinylidene complexes, complexes containing Os/Ru metals are found to have many important applications.[5−10]

Recently, many five-coordinate vinylidene complexes, formulated as M(X)Cl(=C=CHR)L_2 (M = Os/Ru; L = phosphine; X = H, CH=CH($SiMe_3$), C(C≡CCMe_3)=$CHCMe_3$, Cl, etc.), have been synthesized and characterized.[11−16] The majority of these complexes adopt a distorted-trigonal-bipyramidal geometry with the two L's at the apical positions and Cl, vinylidene, and X ligands on the equatorial plane (see **1**). Because of the different substituents on the vinylidene ligand, two vinylidene rotational isomers resulting from the *syn* and *anti* orientations of the R group are possible for each of these vinylidene complexes. An interesting phenomenon is that the vinylidene rotational isomers for some complexes can be observed at low temperature by ^{1}H NMR, while for some other complexes rotational isomers cannot be observed. For example, rotational isomers have been detected at −60 °C for OsHCl(=C=CHPh)(P^iPr_3)$_2$ and Os(C(C≡C^{t}Bu)=CH^{t}Bu)Cl(=C=CH^{t}Bu)(PPh_3)$_2$.[12,13] However, for RuHCl(=C=CHSiMe_3)(P^tBu_2Me)$_2$, RuHCl(=C=CHPh)(P^iPr_3)$_2$, RuHCl(=C=CHPh)(P^tBu_2Me)$_2$, and OsHCl(=C=CHSiMe_3)(P^iPr_3)$_2$, there was no evidence for coexistence of two isomers even down to −90 °C.[14] These observations have prompted us to study the vinylidene rotational barriers of M(X)Cl(=C=CHR)L_2 (M = Os, Ru; L = phosphine; X = SiH_3, SiF_3, H, CH_3, CH=CH_2, Cl; R = H, Ph, SiH_3, SiF_3) and to examine factors influencing the rotational barriers with the aid of density functional theory calculations.



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(1) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193−195*, 977.
(2) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197.
(3) Wolf, J.; Stüer, W.; Grünwald, C.; Werner, H.; Schwab, P.; Schulz, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1124.
(4) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311.
(5) Touchard, D.; Haquette, P.; Guesmi, S.; Pichon, L. L.; Daridor, A.; Toupet, L.; Dixneuf, P. *Organometallics* **1997**, *16*, 3640.
(6) Yang, S.-M.; Chan, M. C.-W.; Cheung, K.-K.; Che, C.-M.; Peng, S.-M. *Organometallics* **1997**, *16*, 2819.
(7) Martin, M.; Gevert, O.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1996**, 2275.
(8) Weber, B.; Steinert, P.; Wundmüller, B.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1994**, 2595.
(9) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105.
(10) Bianchini, C.; Masi, D.; Romerosa, A.; Zanobini, F.; Peruzzini, M. *Organometallics* **1999**, *18*, 2376.
(11) Huang, D. J.; Oliván, M.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 4700.
(12) Bourgault, M.; Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1997**, *16*, 636.
(13) Wen, T. B.; Yang, S. Y.; Zhou, Z. Y.; Lin, Z.; Lau, C. P.; Jia, G. *Organometallics* **2000**, *19*, 3757.
(14) Oliván, M.; Clot, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 897.
(15) Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1997**, *16*, 2227.
(16) Hill, A. F.; Hulkes, A. G.; White, A. J. P.; Williams, D. J. *Organometallics* **2000**, *19*, 371.

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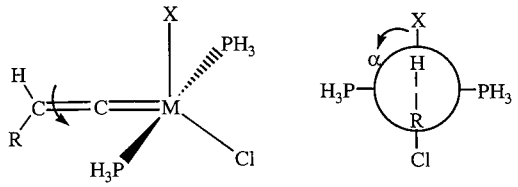
Observations of two rotational isomers in solution largely depend on the magnitude of vinylidene rotational barriers. Smaller barriers make complexes highly fluxional. Therefore, the two rotational isomers of each complex cannot be detected on the NMR time scale.

Computational Details

The model complexes $M(X)Cl(=C=CH_2)(PH_3)_2$ (M = Os, Ru; X = SiF_3, SiH_3, H, $CH=CH_2$, CH_3, Cl) (see **2**) have been used to examine the effects of X and the metal center on the vinylidene rotational barriers. The ligands (X) used here



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represent different electronic properties, including a π-donor (Cl), σ-donors (H, $CH=CH_2$, and CH_3), and π-acceptors (SiH_3 and SiF_3). The effect of substituents at the vinylidene ligand on the rotational barriers has also been studied using the model complexes $OsHCl(=C=CHR)(PH_3)_2$ (R = SiF_3, SiH_3, H, Ph).

Molecular geometries of model complexes have been optimized using the Becke3LYP (B3LYP) level.[17] The LANL2DZ effective core potentials[18] and basis sets were used to describe Ru, Os, P, and Cl, while the standard 6-31G basis set was used for all other atoms.[19] Polarization functions were added for Si (ξ(d) = 0.45). The energies are reevaluated with single-point calculations with the optimized structures using a better basis. In this new basis set, polarization functions are also added for all other nonmetal atoms: i.e., P (ξ(d) = 0.34) and Cl (ξ(d) = 0.514) and 6-31G** for carbon, fluorine, and hydrogen.

The energetics of vinylidene rotation have been investigated by calculating the energies of various rotamers corresponding to different values of dihedral angles α between the plane of the vinylidene ligand and the equatorial plane containing M, X, and Cl. The definition of α is also shown in **2** by a Newman projection.

To examine the effect of basis sets, the better basis set described above was used to perform geometry optimizations for $Os(X)Cl(=C=CH_2)(PH_3)_2$ (X = SiF_3, SiH_3, H, $CH=CH_2$, CH_3, Cl) complexes. The calculated structures are similar to those obtained from the calculations with a medium-sized basis set. The changes in the bond lengths and angles are within 0.02 Å and 2°.

All calculations were performed using the Gaussian 98 software package.[20] In an attempt to support the orbital interaction model presented in the following sections, natural bond orbital (NBO) analyses were performed using the NBO program[21] as implemented in the Gaussian 98 program. The molecular orbitals (Figure 4) obtained from B3LYP results were plotted using the Molden v3.5 program written by Schaftenaar.[22]

Results

In an effort to obtain the rotational barriers of vinylidene ligand for the model complexes $M(X)Cl(=C=CH_2)(PH_3)_2$ (M = Os, Ru; X = SiF_3, SiH_3, H, $CH=CH_2$, CH_3, Cl), the most stable conformations have been fully optimized first. The results show that the most stable conformations of model complexes correspond to a coplanar structure of the vinylidene ligand plane and the equatorial plane containing M, X, and Cl. The dihedral angle α between the two planes is ca. 0°. The optimized geometries of model complexes $M(X)Cl(=C=CH_2)(PH_3)_2$ with different metals and X ligands are shown in the left-hand columns of Figures 1 and 2. In Figures 1 and 2, the two phosphine ligands of each model complex are almost perpendicular to the plane containing metal, X, and Cl for both the most stable conformation and the transition-state structure and, therefore, are omitted from the figures for the purpose of clarity. The calculated structural parameters of the model complexes $\mathbf{4^{Os}}$ and $\mathbf{6^{Ru}}$ (see Figures 1 and 2 for the numbering schemes) are compared with those (given in parentheses) available from the experimentally X-ray determined structures of $Os[CH=CH(SiMe_3)]Cl[=C=CH(SiMe_3)](P^iPr_3)_2$ and $RuCl_2(=C=CHPh)(PCy_3)_2$.[11,23] The agreement between the calculated and experimental parameters is reasonably good, particularly for the metal−vinylidene structural units.

The geometries of vinylidene ligand rotamers corresponding to different values of rotational angle α have also been calculated. For each fixed value of α, the rest of the geometry was relaxed. The energies corresponding to different rotamers were calculated. The rotational potential energy surfaces for the model complexes $M(X)Cl(=C=CH_2)(PH_3)_2$ (M = Os, Ru; X = SiF_3, SiH_3, H, $CH=CH_2$, CH_3, Cl) showing the change in relative energy with respect to α have been obtained. The potential energy surfaces are all similar, and only two of them corresponding to $Os(X)Cl(=C=CH_2)(PH_3)_2$ (X = SiF_3, CH_3) are shown in Figure 3. Obviously, the highest energy conformations which are the transition states along the vinylidene rotational path correspond to α = 90°. Frequency calculations confirm that the structures at α = 90° are indeed transition states. The imaginary frequency corresponding to the rotation of the vinylidene ligand is -318 cm^{-1} for $Os(CH_3)Cl(=C=CH_2)(PH_3)_2$ and -209 cm^{-1} for $Os(SiF_3)Cl(=C=CH_2)(PH_3)_2$. The structures of transition states for all model complexes are shown in the right-hand columns of Figures 1 and 2. The vinylidene rotational barrier for each model complex is the energy difference between the pair of structures shown in Figures 1 and 2 for each complex.

(17) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (c) Lee, C.; Yang, W.; Parr, G. *Phys. Rev. B* **1988**, *37*, 785.
(18) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(19) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; *Gaussian 98 (Revision A.7)*; Gaussian, Inc.: Pittsburgh, PA, 1998.
(21) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO (version 3.1)*.
(22) Schaftenaar, G. *Molden v3.5*; CAOS/CAMM Center Nijmegen; Toernooiveld, Nijmegen, The Netherlands, 1999.
(23) Wolf, J.; Stüer, W.; Grünwald, C.; Gevert, O.; Laubender, M.; Werner, H. *Eur. J. Inorg. Chem.* **1998**, 1827.

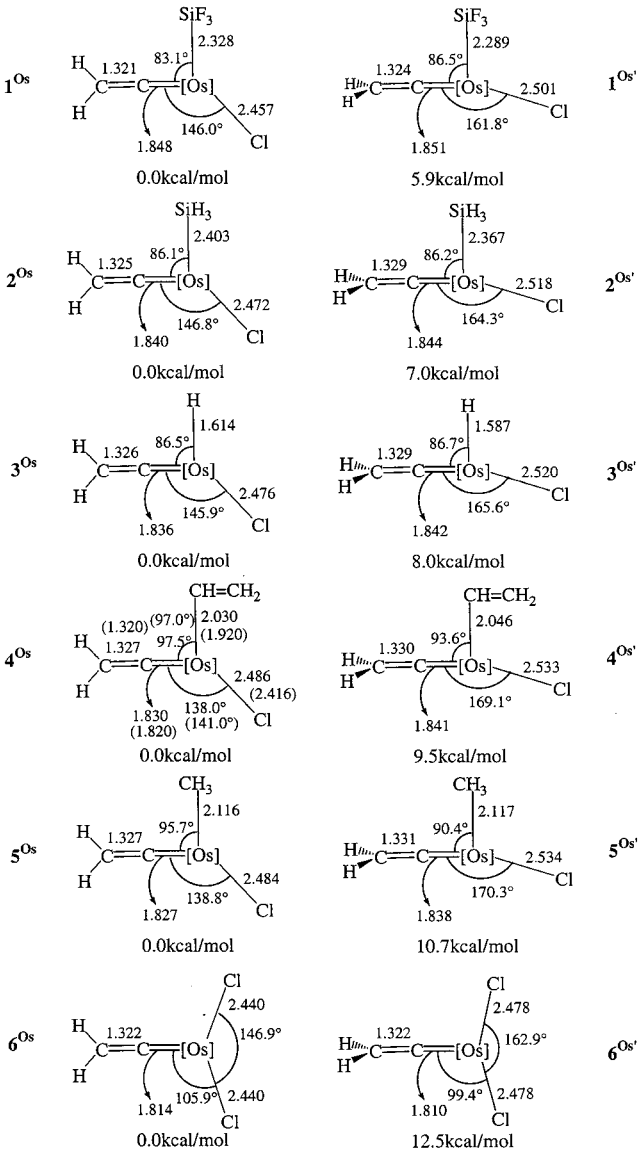

Figure 1. Calculated structures together with the relative energies of the most stable conformations (left-hand column) and the corresponding vinylidene rotational transition states (right-hand column) for the model complexes Os(X)Cl(=C=CH_2)(PH_3)$_2$. The PH_3−Os−PH_3 structural unit of each complex is perpendicular to the molecular plane shown in the figure, and the two PH_3 ligands are omitted for clarity.

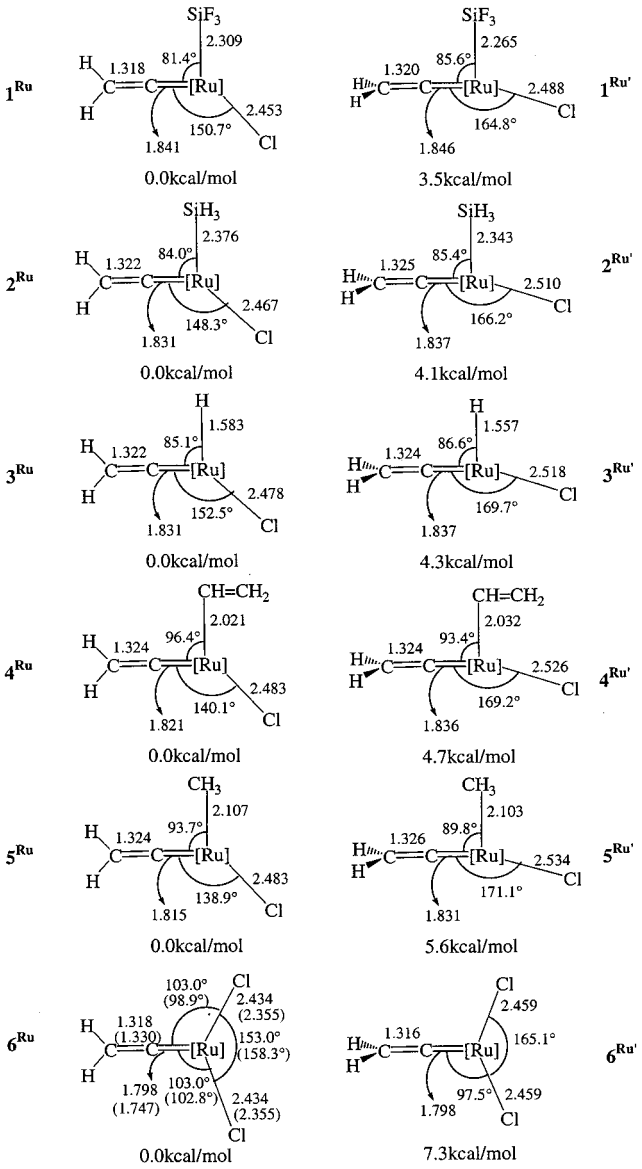

Figure 2. Calculated structures together with the relative energies of the most stable conformations (left-hand column) and the corresponding vinylidene rotational transition states (right-hand column) for the model complexes Ru(X)Cl(=C=CH_2)(PH_3)$_2$. The PH_3−Ru−PH_3 structural unit of each complex is perpendicular to the molecular plane shown in the figure, and the two PH_3 ligands are omitted for clarity.

The rotational barriers of all model complexes are also listed in Table 1 for comparison.

From Table 1, we can see that the vinylidene rotational barriers increase with X from having π-acceptor, σ-donor to having π-donor properties. In the literature, the vinyl (−CH=CH_2) ligand has been considered as a single-face π-acceptor.[24,25] In the complexes studied here, the vinyl ligand is always coplanar with the equatorial plane. In such an orientation, the metal d orbital used for a back-bonding interaction with the vinyl ligand is d_δ-type with respect to the vinylidene ligand. The single-face π-acceptor property does not play a role in determining the rotational barrier. Therefore, the vinyl ligand is considered to mainly act as a σ-donor. We can also see that the rotational barriers for Os complexes are generally higher than those of the Ru analogues. The vinylidene rotational barriers for MHCl(=C=CH_2)(PH_3)$_2$ (M = Os, Ru) have been calculated.[14] It was also found that the barrier for the Os complex (8.1 kcal/mol) is higher than that for the Ru complex (4.3 kcal/mol). In the following section, the detailed structural changes from the most stable conformation to the transition state for each complex will be discussed in order to understand the trends observed.

The effect of the substituent R on the vinylidene ligand has been studied using the model complexes OsHCl(=C=CHR)(PH_3)$_2$ (R = SiF_3, SiH_3, H, Ph). A similar calculation method is used to obtain the rotational barriers. The calculated rotational barriers of

(24) Choi, S.-H.; Bytheway, I.; Lin, Z.; Jia, G. *Organometallics* **1998**, *17*, 3974.

(25) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

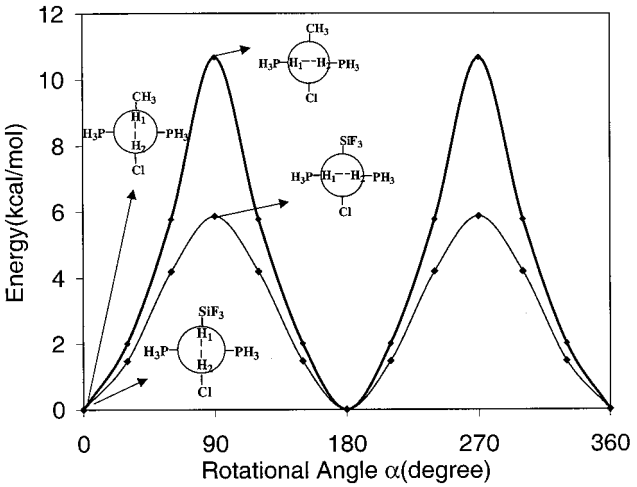

Figure 3. Potential energy surfaces for Os(X)Cl(=C=CH_2)(PH_3)$_2$ (X = CH_3, SiF_3) showing the changes in relative energies (kcal/mol) with respect to α (deg). Newman projections showing the relative orientations of the vinylidene ligand within the complexes are given on the most stable conformations and the transition states.

Table 1. Rotational Barriers (kcal/mol) of Vinylidene Ligands of the Model Complexes M(X)Cl(=C=CH_2)(PH_3)$_2$ and OsHCl(=C=CHR)(PH_3)$_2$ with Different Ligands X, Metals M and Substituents R of Vinylidene Ligands

M(X)Cl(=C=CH_2)(PH_3)$_2$		
	barrier	
X	M = Os	M = Ru
SiF_3	5.9	3.5
SiH_3	7.0	4.1
H	8.0	4.3
CH=CH_2	9.5	4.7
CH_3	10.7	5.6
Cl	12.5	7.3

OsHCl(=C=CHR)(PH_3)$_2$	
R	barrier
SiF_3	4.2
SiH_3	6.2
H	8.0
Ph	8.2

OsHCl(=C=CHR)(PH_3)$_2$ (R = SiF_3, SiH_3, H, Ph) are also listed in Table 1. The results show that the rotational barriers also increase with the electron donation abilities of R.

Discussion

Structural Aspects of Model Complexes. Before discussing the vinylidene rotational barriers for various model complexes, we briefly summarize the calculated structures of model complexes M(X)Cl(=C=CH_2)(PH_3)$_2$.

The most stable conformations (see left-hand columns of Figures 1 and 2) can be described as distorted-trigonal-bipyramidal structures with the two L ligands at the apical positions and Cl, vinylidene, and X ligands on the equatorial plane. For 16-electron ML_5 complexes, it has been found that both square-pyramidal and distorted-trigonal-bipyramidal (also called Y-shape) structures are possible due to the Jahn−Teller effect.[15,26,27] The presence of a π-donor ligand is found necessary to give a Y-shaped structure. Most of the studied complexes here have adopted Y-shaped structures with the Cl ligand at the foot of the Y geometry, except for **6**^{Os} and **6**^{Ru}, which are better described as square-pyramidal and will be discussed later. The adoption of Y-shaped structures for vinylidene complexes has been discussed in detail in the literature.[15]

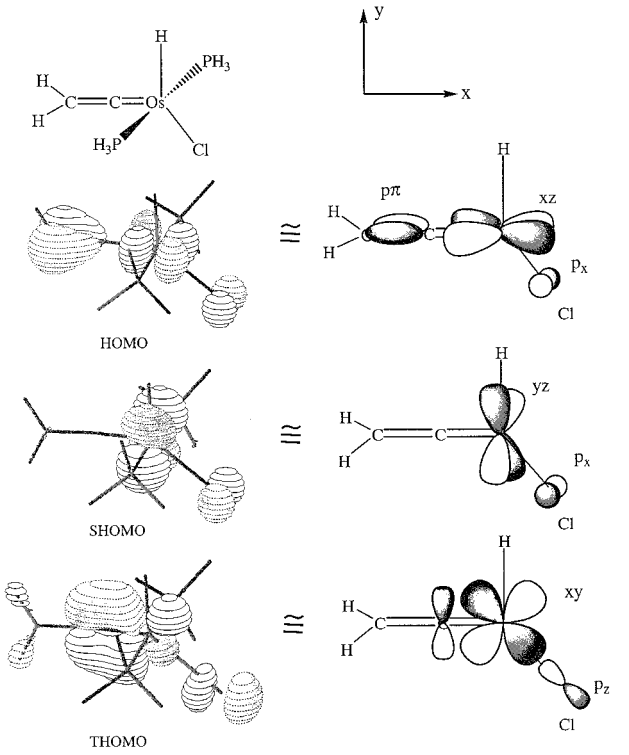

Figure 4. Spatial plots of the three highest occupied molecular orbitals (HOMO, SHOMO, and THOMO) for the most stable conformation of OsHCl(=C=CH_2)(PH_3)$_2$. The molecular orbitals were obtained from the B3LYP calculations.

The studied complexes here can be formally described as d^6 complexes if we consider the vinylidene ligands to be neutral, single-face (one empty p orbital) π acceptors. The molecular orbital calculation for OsHCl(=C=CH_2)(PH_3)$_2$ shows that the three orbitals which accommodate the six d electrons correspond to the three highest occupied molecular orbitals, shown in Figure 4. Examinations of other model complexes give the same result. The third HOMO (THOMO) represents the metal−C(vinylidene) d−p π-bonding interaction with some slight σ-antibonding interaction with the Cl ligand. The second HOMO (SHOMO) is the d_{yz} orbital, which is slightly π-antibonding with Cl, and the HOMO is the d_{xz} orbital, which is slightly π-antibonding with Cl and the C=C π orbital of the vinylidene ligand (see Figure 4 for the Cartesian coordinates). The slightly antibonding feature is a result of π-donor properties of the two ligands.

The geometries for the transition states along the vinylidene rotational paths are typical square-pyramidal

(26) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729.
(27) Rachidi, I. E.-I.; Eisenstein, O.; Jean, Y. *New J. Chem.* **1990**, *14*, 671.

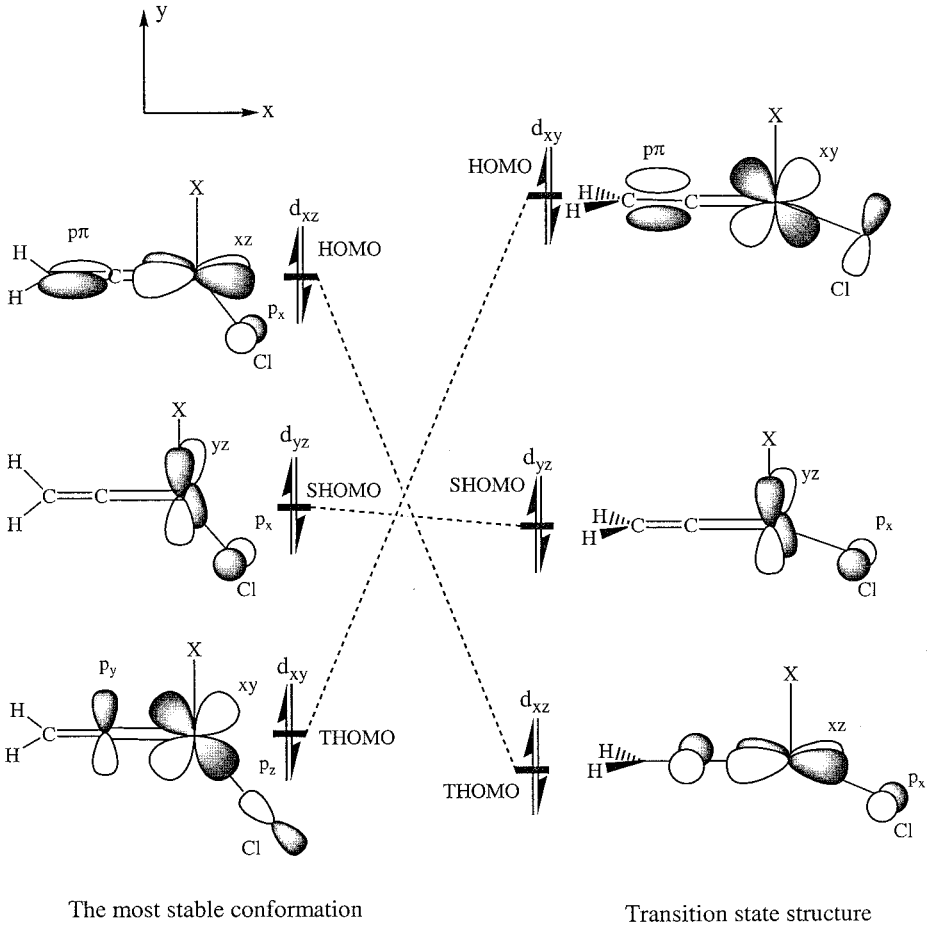

Figure 5. Schematic orbital correlation diagram showing the three highest occupied molecular orbitals for the most stable conformation and the transition state of the model complex $M(X)Cl(=C=CH_2)(PH_3)_2$.

structures, which are also called T-shaped (see the right-hand columns of Figures 1 and 2). Comparing the most stable conformations and the corresponding rotational transition states, we can see that the Cl ligands slide away from the vinylidene ligands on the equatorial plane accompanying the rotation of vinylidene ligands.

In the transition structures, the metal−vinylidene π bonding interaction involves the d_{xz} orbital. Because of the bonding interaction, the d_{xz} orbital becomes the third HOMO. The sliding of Cl by increasing the Cl−M−vinylidene angle in the transition structures weakens the overall metal−vinylidene bond, since the chlorine ligand now occupies the trans position of the vinylidene ligand. Except for X = Cl, the calculated metal−vinylidene bond distances are clearly longer in the transition structures than in the corresponding most stable conformations. Although an increase in the Cl−M−vinylidene angle causes unfavorable effects on the metal−vinylidene interactions, the angle increase, however, alleviates the d_{yz}−p_x(Cl) antibonding interaction. Figure 5 summarizes the orbital energy changes from the most stable conformation to the transition structure for the three d orbitals which accommodate the six d electrons.

When X = Cl, one has the dichloride complexes $MCl_2(=C=CH_2)(PH_3)_2$ (**6**^{Os} and **6**^{Ru}). Both the most stable conformations and the corresponding transition structures adopt a square-pyramidal structure in which the two vinylidene−metal−chloride angles are equal. The adoption of the high-symmetry structure is probably due to the two chloride ligands competing equally for bonding with the metal center. The Cl−M−Cl angle in the most stable conformation is calculated to be smaller when compared with that in the transition structure. The smaller Cl−M−Cl angle in the most stable conformation (see **6**^{Os} or **6**^{Ru}) is a result of using the in-plane d orbital for metal−vinylidene π bonding. The two chlorides bend away from the vinylidene ligand, enhancing the metal−vinylidene π interaction. For the corresponding transition structure (see **6**$^{Os'}$ or **6**$^{Ru'}$), the Cl−M−Cl angle is larger because the metal−vinyldene π bonding uses the d orbital on the vinylidene−metal−phosphine plane.

Effect of X Ligands on the Rotational Barriers of Vinylidene Ligands. Table 1 shows that the vinylidene rotational barriers of $M(X)Cl(=C=CH_2)(PH_3)_2$ (M = Os/Ru; X = SiF_3, SiH_3, H, $CH=CH_2$, CH_3, Cl) increase with X from having π-acceptor, σ-donor to having π-donor properties. Before discussing how ligands X influence the rotational barriers, it is necessary to summarize the relevant structural changes. The calculated metal−C(vinylidene) bond distances decrease with the increase of π-donor properties of X (see the trend along the series of X in Table 2). The corresponding bond indices, also listed in Table 2, show a similar trend. In other words, ligands X with π electron-donor properties enhance the metal−vinylidene bonding. A plausible explanation for the trend is that complexes with a π-acceptor X experience unfavorable metal−vinylidene

Table 2. Calculated Wiberg Bond Indices (from NBO) and Bond Lengths of M−C(vinylidene) in the Model Complexes M(X)Cl(=C=CH_2)(PH_3)$_2$

X	Wiberg bond index	bond length (Å)
	Os(X)Cl(=C=CH_2)(PH_3)$_2$	
SiF_3	1.405	1.848
SiH_3	1.436	1.840
H	1.488	1.836
CH=CH_2	1.493	1.830
CH_3	1.514	1.827
Cl	1.575	1.814
	Ru(X)Cl(=C=CH_2)(PH_3)$_2$	
SiF_3	1.294	1.841
SiH_3	1.343	1.831
H	1.369	1.830
CH=CH_2	1.390	1.821
CH_3	1.422	1.815
Cl	1.493	1.798

π bonding interactions since the π-acceptor X competes for the metal-to-ligand back-donation.

Examining the structural changes from the most stable structure to the transition state, we found that both the metal−C(vinylidene) and metal−chloride bond distances are lengthened. The lengthening can be reasonably related to the *trans* influence due to the *trans* arrangement of the vinylidene and chloride ligands in the transition state structures. The changes in the M−X distances from the most stable conformations to transition states, however, are found to vary, depending on the type of X ligand. The metal−silyl bond distances are significantly shortened. The M−H bond distances are also shortened, while the M−CH_3 bonds remain almost unchanged. The M−vinyl bonds, however, are lengthened. On one hand, the sliding away of Cl from the *trans* position of X from the most stable conformation to the transition state should enhance the M−X bonding due to the absence of the *trans* influence. On the other hand, the sliding creates steric crowding for the metal−X bonding interaction. Therefore, a final compromise is that the M−H bonds are shortened due to the small size of H. The M−CH_3 distances remain almost unchanged, while the metal−vinyl distances are lengthened because of the bulky nature of the vinyl ligand. The significant shortening observed for the metal−silyl bonds from the most stable conformations to transition states should have other electronic factors in addition to the reducing *trans* influence mentioned above. The d orbital used for the metal−vinylidene π bonding in the transition state is mainly d_δ-type in nature with respect to X (see d_{xz} on the right-hand side of Figure 5). It is expected that the π-acceptor X is able to stabilize the HOMO significantly and, therefore, enhances the M−X interaction. Summarizing all the factors influencing the transition states, we can assume that the smaller barriers for complexes with silyl ligands (X) are related to the stabilization effect of the π-acceptor on the HOMO (d_{xy}) in the transition states. Similarly, the higher barriers for the dichloride complexes (**6**^{Os} and **6**^{Ru}) can be related to the destabilizing effect of the π-donor (Cl) on the d_{xy} (HOMO) orbital. We conclude here that π-acceptor ligands (X) play the stabilizing role in the transition structure and, therefore, reduce the corresponding rotational barriers.

Table 3 lists the HOMO−LUMO gaps as well as the orbital energies of HOMOs for various osmium model complexes. Stronger π-acceptor ligands X indeed give lower HOMO orbital energies. The energy differences (ΔHOMO) between the HOMOs of the most stable structures and their corresponding transition states increase with the π electron donating ability of X (see Table 3). The HOMO−LUMO gap differences (ΔGap) between the most stable structures and their corresponding transition states also show a similar trend. These trends provide quantitative support to the conclusion that stronger π-acceptor ligands (X) relatively stabilize the HOMOs of the transition structures, giving smaller vinylidene rotational barriers.

Table 3. Orbital Energies (in au) of HOMOs, HOMO−LUMO Gaps, ΔHOMO, and ΔGap of the Most Stable Conformations and Transition Structures for the Model Complexes Os(X)Cl(=C=CH_2)(PH_3)$_2$ and OsHCl(=C=CHR)(PH_3)$_2$[a]

	most stable conformation		transition structure			
	HOMO	HOMO−LUMO gap	HOMO	HOMO−LUMO gap	ΔHOMO	ΔGap
	Os(X)Cl(=C=CH_2)(PH_3)$_2$					
SiF_3	−0.224	0.131	−0.211	0.131	0.013	0.000
SiH_3	−0.209	0.129	−0.191	0.122	0.018	0.007
H	−0.201	0.133	−0.182	0.122	0.019	0.011
CH=CH_2	−0.203	0.138	−0.181	0.121	0.022	0.017
CH_3	−0.201	0.137	−0.176	0.116	0.025	0.021
Cl	−0.223	0.137	−0.193	0.112	0.030	0.025
	OsHCl(=C=CHR)(PH_3)$_2$					
SiF_3	−0.227	0.139	−0.211	0.134	0.016	0.005
SiH_3	−0.209	0.134	−0.191	0.127	0.018	0.007
H	−0.201	0.133	−0.182	0.122	0.019	0.011
Ph	−0.187	0.109	−0.175	0.107	0.012	0.002

[a] ΔHOMO is the orbital energy difference between the HOMO of the most stable structure and its corresponding transition state. ΔGap is the energy difference between HOMO−LUMO gaps of the most stable structure and its corresponding transition state.

Following the suggestion of one reviewer, we have also examined the changes of charge population on X from the most stable structures to their transition structures. We found no significant changes in the population. In addition, no clear correlation along the series of ligands X can be observed. These observations further support the notion that the stabilization on the relevant HOMOs seems to be the most important.

Effect of Metal Centers. The calculated rotational barriers for Os complexes are generally higher than those of the Ru analogues (see Table 1). This result is consistent with the periodic trend that osmium has more diffuse d orbitals than ruthenium does. Because of the more diffuse d orbitals, osmium is expected to have stronger interactions with ligands. Therefore, the stabilizing/destabilizing effects discussed above should be greater for osmium complexes than for ruthenium complexes. As a result, the osmium complexes have higher vinylidene rotational barriers.

Effect of Substituents R. Calculations for the model complexes OsHCl(=C=CHR)(PH_3)$_2$ (R = SiF_3, SiH_3, H, Ph) show that the vinylidene rotational barriers also increase with the π electron-donating abilities of substituents R (see Table 1). It appears that the barriers for complexes with silyl substituents are lower. This result is consistent with the experimental observation that rotational isomers have been observed for OsHCl(=C=CHPh)(P^iPr_3)$_2$ but not for OsHCl(=C=CHSiMe_3)(P^iPr_3)$_2$.[12,14] Figure 6 shows the calculated structures

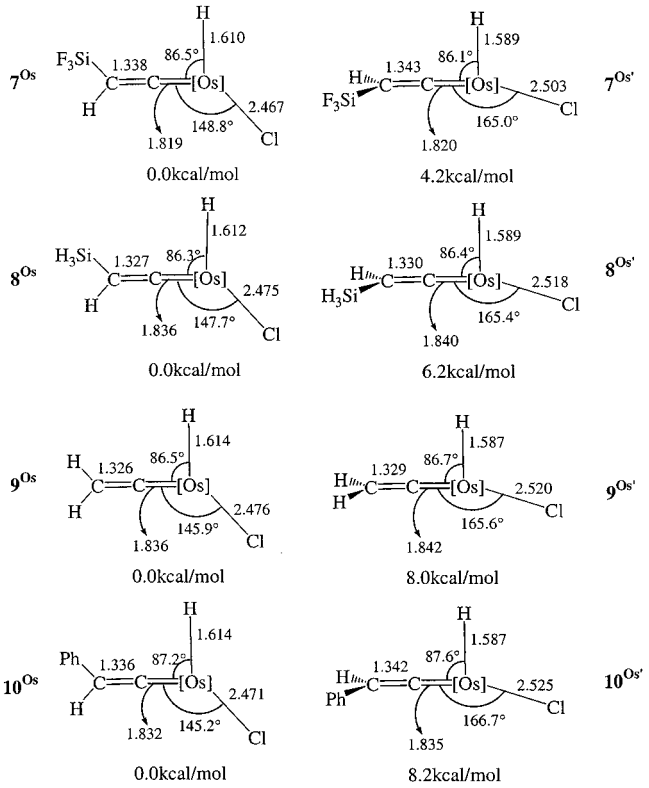

Figure 6. Calculated structures together with the relative energies of the most stable conformations (left-hand column) and the corresponding vinylidene rotational transition states (right-hand column) for the model complexes $OsHCl(=C=CHR)(PH_3)_2$. The $PH_3-Os-PH_3$ structural unit of each complex is perpendicular to the molecular plane shown in the figure, and the two PH_3 ligands are omitted for clarity.

ofthe most stable conformations and the corresponding transition states. The structural changes from the most stable conformations to transition states in those calculated complexes are similar to those discussed above. The Os−vinylidene and Os−Cl distances are lengthened, while the Os−H bonds are shortened. In the preceding section, we have seen that ligands X with π-acceptor properties can stabilize the transition structures through their orbital interactions (metal-to-ligand back-donation) with the metal d_{xy} orbital in the HOMO by alleviating the antibonding interactions with other ligands (see the d_{xy} orbital on the right-hand side of Figure 5). Substituents R with π electron-withdrawing properties, such as silyl groups, stabilize the C−C π bonding orbital of the vinylidene ligand, reducing its antibonding interaction with the d_{xy} orbital in the HOMO. In other words, silyl groups can also stabilize the HOMO in the transition structures of these complexes. Therefore, complexes with silyl substituents are calculated to have smaller vinylidene rotational barriers.

The stabilizing effect of the silyl groups also finds support from their lower HOMO orbital energies and their larger HOMO−LUMO gaps (see Table 3). Except for the case when R = Ph, the trends in the ΔHOMO and ΔGap values are also similar to those discussed above when the effect of ligands X was examined. The exception is not very clear and may be related to the fact that several π orbitals of the phenyl group are involved in the orbital interactions with the C−C π bond of the vinylidene ligand. Therefore, more molecular orbitals in addition to the HOMO have to be considered.

Summary

The rotational barriers of vinylidene ligands of five-coordinate complexes $M(X)Cl(=C=CHR)L_2$ (M = Os, Ru; L = phosphine) have been investigated by density functional theory calculations. The effects of X, transition metal M, and substituent R of vinylidene ligand have been examined.

In the most stable conformations, the model complexes $M(X)Cl(=C=CH_2)(PH_3)_2$ (M = Os, Ru; X = SiF_3, SiH_3, H, $CH=CH_2$, CH_3) adopt Y-shaped structures. With the rotation of the vinylidene ligands by 90°, the Cl ligands slide to the *trans* position with respect to the vinylidene ligands, and the geometries of the model complexes become T-shaped structures. The $MCl_2(=C=CH_2)(PH_3)_2$ complexes adopt a square-pyramidal structure in both the most stable conformation and transition state, except for the changes of Cl−M−Cl angles.

The rotational barriers of the vinylidene ligand are found to increase with X from π acceptor, σ donor to π donor properties. Ligands (X) with π-acceptor properties stabilize the transition structures through interactions with the d orbital in the HOMO, which is used for the metal−vinylidene π bonding in the most stable conformations.

Complexes with silyl substituents on the vinylidene ligand are found to have smaller rotational barriers. The π-acceptor properties of the silyl group are also capable of stabilizing the HOMO in the transition structures.

The calculated rotational barriers for Os complexes are generally higher in comparison to the Ru analogues. The strong metal−ligand interactions for osmium due to its more diffuse d orbitals are responsible for the higher rotational barriers.

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