Organometallics **1999,** *18,* 2473−2478

Structural Preferences in η^2-Alkenyl Transition-Metal Complexes $ML_5(\eta^2$-alkenyl) and $MCpL_2(\eta^2$-alkenyl)

Sai-Heung Choi and Zhenyang Lin*

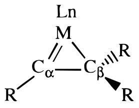
Department of Chemistry, The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong

Received January 19, 1999

Density functional molecular orbital calculations have been used to study the preference for coplanarity of the η^2-alkenyl and one of the metal−ligand bonds in transition-metal η^2-alkenyl complexes. The metal−η^2-alkenyl bonding in these complexes involves the Dewar−Chatt−Duncanson type of interactions (the donation of η^2-alkenyl π electrons to the metal center and the metal(d)−η^2-alkenyl(π^*) back-donation) and metal(d)−C_α(p) π bonding. The Dewar−Chatt−Duncanson type of interactions is found to be the dominant factor in determining the structural preference while the metal−C_α π bonding strength remains approximately constant with respect to the η^2-alkenyl rotation. When the C_α−C_β vector of the η^2-alkenyl ligand eclipses (is coplanar with) one of the metal−ligand bonds, the metal−η^2-alkenyl interactions are the strongest because the mixing of metal d−p orbitals, resulting from the metal−ligand distortion, enhances the metal(d)−η^2-alkenyl(π^*) back-donation. For η^2-alkenyl complexes containing a Cp ligand, the steric effect of the bulky Cp ligand is also operative although the electronic factors are still dominant in determining the structural preference.

Introduction

Transition-metal η^2-alkenyl complexes $ML_n(\eta^2\text{-}C_2R_3)$, are normally described as metallacyclopropenes,[1] which contain both metal−carbon single and double bonds as illustrated in **1**. These complexes are of considerable interest because a variety of catalysis, such as alkyne oligomerization,[2] alkyne cyclization, carbonylation,[3] and hydrodesulfurization,[4] postulate the crucial participation of η^2-alkenyl intermediates. In these catalytic processes, the η^2-alkenyl ligand is thought to stabilize the metal center,[5] and the interconversion of its hapticity from η^2 to η^1 is involved. Research efforts trying to understand the relevant catalytic processes over the last two decades have led to the syntheses and characterization of numerous transition-metal η^2-alkenyl complexes. Examples of these complexes are listed in Table 1.[6−13]



1

Table 1. Examples of Transition-Metal η^2-alkenyl Complexes and Their Corresponding η^2-Alkenyl−Metal−Ligand Dihedral Angles θ^a

complex	dihedral angle θ (deg)	ref
$ML_5(\eta^2$-alkenyl) Complexes		
$W(CO)(I)[CN(2,6\text{-}C_6H_3Me_2)](PMe_3)_2(\eta^2\text{-}CPhC{=}S)$	5.5	11
$\{Re(Cl)[PPh_2(CH_2)_2PPh_2]_2[\eta^2\text{-}C(CH_2Ph)CH_2]\}^+$	8.1	12
$W(CO)(PPh_3)[HB(pz)_3]\ [\eta^2\text{-}C(p\text{-}Tol)C{=}O]$	8.7	13
$MCpL_2(\eta^2$-alkenyl) Complexes		
$CpMo[P(OMe)_3]_2[\eta^2\text{-}C(t\text{-}Bu)CHPh]$	4.4	6
$\{CpRe[PPh_2(CH_2)_2PPh_2]_2(\eta^2\text{-}CPhCHPh)\}^+$	10.8	7
$(\eta^5\text{-}C_9H_7)Mo[P(OMe_3)]_2(\eta^2\text{-}CSiMe_3CH_2)$	13.8	8
$CpWCl(CF_3C{\equiv}CCF_3)[\eta^2\text{-}CF_3CC(CF_3)(PEt_3)]$	17.4	9
$CpMo[P(OMe)_3]_2(\eta^2\text{-}CPhCHPh)$	19.6	6
$CpW(CO)_2[\eta^2\text{-}CF_3CC(CF_3)(-C({=}O)SMe)]$	165.8	10
$CpMo[P(OMe)_3]_2(\eta^2\text{-}CMeCPh_2)$	179.5	6
$CpRe(PPh_2Me)(Br)(\eta^2\text{-}CPhCHPh)$	200.1	7

[a] Abbreviations used: Me = methyl; *t*-Bu = *tert*-butyl; Et = ethyl; Ph = phenyl; pz = pyrazol-1-yl; *p*-Tol = *p*-toluene.

Complexes in Table 1 all have *pseudo*-octahedral structures if one assumes that the cyclopentadienyl (Cp) ligand occupies one face of the octahedron and the η^2-alkenyl ligand occupies a single coordination site. Examining the detailed structures of these η^2-alkenyl

---

(1) (a) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 78. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley: New York, 1994; p 169, 196.

(2) Carlton, L.; Davidson, J. L.; Ewing, P.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1474.

(3) Davidson, J. L.; Vasapollo, G.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1025.

(4) Spera, M. L.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 8843.

(5) (a) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley-Interscience: New York, 1992.

(6) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435.

(7) Carfagna, C.; Carr, N.; Deeth, R. J.; Dossett, S. J.; Green, M.; Mahon, M. F.; Vaughan, C. *J. Chem. Soc., Dalton Trans.* **1996**, 415.

(8) Allen S. R.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 826.

(9) Davidson, J. L.; Wilson, W. F.; Manojlovic-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1983**, *254*, C6.

(10) Davidson, J. L.; Shiralian, M. *J. Chem. Soc., Dalton Trans.* **1984**, 2167.

(11) Lee, T.-Y.; Mayr, A. *J. Am. Chem. Soc.* **1994**, *116*, 10300.

(12) Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L.; Silvestre, J.; Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1986**, 1125.

(13) Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 693.

10.1021/om990024i CCC: $18.00

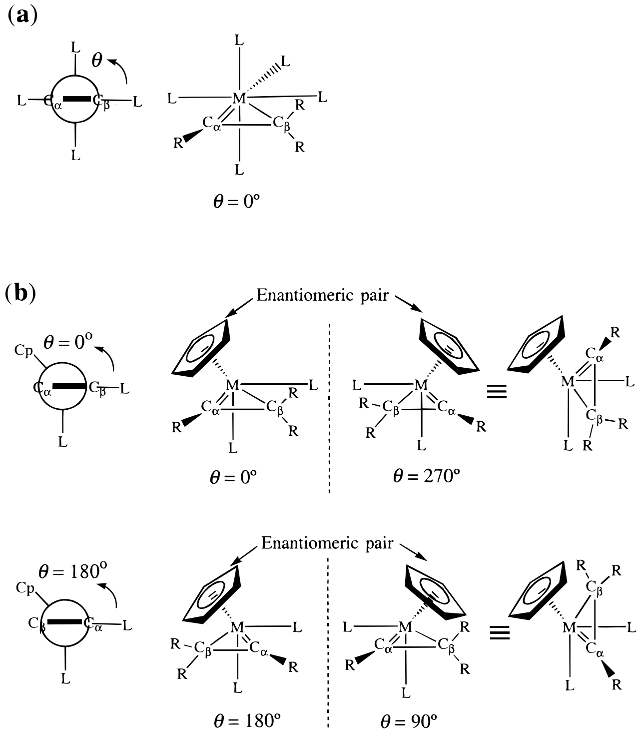


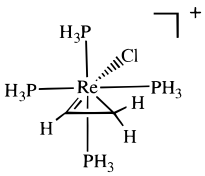
Figure 1. (a) Newman projection diagram showing the orientation of η^2-alkenyl ligand in $ML_5(\eta^2$-alkenyl) complexes. **(**b**)** Newman projection diagram of showing the orientation of η^2-alkenyl ligand in $MCpL_2(\eta^2$-alkenyl) complexes. Conformations with $\theta = 0°$ and 180° together with their enantiomeric isomers are also shown.

complexes, we found that the $C_\alpha-C_\beta$ vector of the η^2-alkenyl ligand in these complexes prefers to eclipse (be coplanar with) one of the metal−ligand vectors (M−L). Here, C_α is defined as the M═C double bond carbon and C_β is assigned as the M−C single bond carbon (see **1**). The dihedral angle θ, $C_\beta-C_\alpha-M-L$, is used to define the $C_\alpha-C_\beta$ vector orientation with respect to the relevant M−L bond. Newman projection diagrams are shown in Figures 1a and 1b for the definition of θ for the cases of η^2-alkenyl complexes without and with a Cp ligand, respectively. For the three complexes which do not contain a Cp ligand, their dihedral angles (θ) are close to 0°. For those complexes containing a Cp ligand (Figure 1b), the structural preference for which the $C_\alpha-C_\beta$ vector of the η^2-alkenyl ligand eclipses one of the M−L bonds is observed. In other words, two preferred conformations in which the dihedral angle θ is close to either 0° or 180° are found (Table 1). Figure 1b also shows that conformations with $\theta = 0°$ and $\theta = 270°$ are enantiomeric pair, and so are those with $\theta = 180°$ and $\theta = 90°$.

Although the structural preference in these transition-metal η^2-alkenyl complexes was mentioned and its metal-(η^2-alkenyl) interaction was discussed in previous studies,[6,7,9,10,14] no explicit explanation for the preference has yet been given. In a previous paper, we have satisfactorily explained the (η^1-alkenyl)−carbonyl coplanarity in terms of a simple molecular orbital model. Continuing our effort in understanding the metal−(η^2-alkenyl) interactions, in this paper, the structural orientation of the η^2-alkenyl ligand in these complexes will be discussed with the aid of quantum chemical calculations. Molecular orbital interaction models will be presented to provide qualitative explanations. In the following sections, the structural preference of transition-metal η^2-alkenyl complexes will be discussed by structural type, namely complexes with and without a Cp ligand. The energetics of η^2-alkenyl rotation will also be examined.

Computational Details

Geometry optimizations were performed at the Becke3LYP (B3LYP) level for all model complexes in which alkyl groups are replaced by hydrogen atoms for theoretical simplicity. The effective core potentials (ECPs) of Wadt and Hay[16] with a double-ξ valence basis were used for chlorine, phosphorus, and transition-metal atoms. The standard 6-31G basis set was used for other atoms.[17] To investigate the energetics of η^2-alkenyl rotation, the models were optimized except for the dihedral angle θ, which was fixed at various values. The effect of polarization functions was also examined for the $[Re(Cl)(PH_3)_4(\eta^2\text{-}CHCH_2)]^+$ **2** system with a larger basis set. The 6-31G* basis set was used for carbon and hydrogen atoms while polarization functions were added for chlorine ($\xi_d = 0.514$) and phosphorus ($\xi_d = 0.340$).[18] A triple-ξ representation of the 5d electrons is derived by splitting the rhenium ECP basis set. Geometry optimizations of the model system **2** were performed with this larger basis set. The results of calculations indicate that the energetics of η^2-alkenyl rotation do not change significantly upon inclusion of these extra polarization functions. The barrier of η^2-alkenyl rotation changes only slightly from 3.7 to 3.0 kcal/mol. The structural parameters involving the metal−(η^2-alkenyl) unit are almost unchanged. The changes in other structural parameters are also small. The bond lengths are within 0.04 Å, and the bond angles are within 1°.



2

All calculations were carried out using the Gaussian 94 package[19] on a Silicon Graphics Indigo² workstation. In an attempt to support the orbital interaction model presented in the following sections, natural bond prder (NBO) analyses were performed using the NBO program[20] as implemented in the Gaussian 94 package.

Results and Discussion

General Considerations. As mentioned above, all complexes considered here can be described as *pseudo*-octahedral structures. Therefore, it is useful to consider

---

[14] Brower, D. C.; Birdwhistell, K. R.; Templeton, J. L. *Organometallics* **1986**, *5*, 94.

[15] Choi, S.-H.; Bytheway, I.; Lin, Z.; Jia, G.*Organometallics* **1998**, *17*, 3974.

[16] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

[17] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[18] Andzelm, J.; Huzinaga, S. *Gaussian Basis Sets for Molecular Calculations*; Elsevier: New York, 1984.

[19] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; *Gaussian 94 (Revision E.2)*; Gaussian, Inc.: Pittsburgh, PA, 1995.

[20] Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO version 3.1.

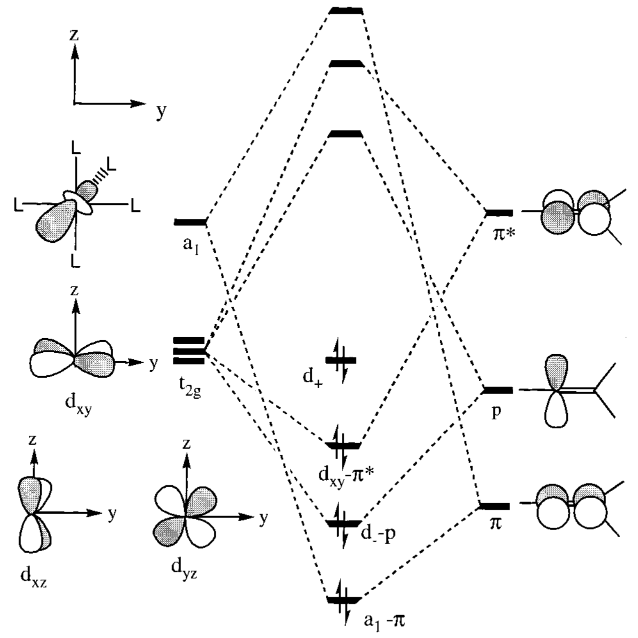
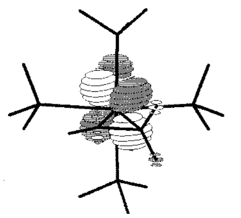


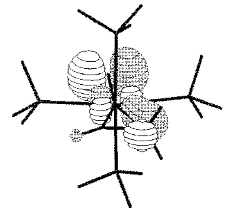
Figure 2. Schematic orbital interaction diagram showing the interactions between an ML_5 fragment and an η^2-alkenyl ligand for an $ML_5(\eta^2\text{-alkenyl})$ complex. In the figure, the d_+ orbital represents the linear combination of $d_{xz} + d_{yz}$ while the d_- orbital represents the linear combination of $d_{xz} - d_{yz}$.

a schematic orbital interaction between an ML_5 fragment and an η^2-alkenyl ligand (Figure 2). The frontier orbitals of an ML_5 fragment consist of an "a_1" and the so-called "t_{2g}" set orbitals. The η^2-alkenyl ligand has π, p, and π^* orbitals, shown in the right column of Figure 2, available for interaction with the metal center. Figure 2 shows that the π orbital of the η^2-alkenyl ligand interacts with the "a_1" frontier orbital of the ML_5 fragment while its π^* orbital overlaps with the d_{xy} orbital. The p orbital on C_α of the η^2-alkenyl ligand mainly interacts with d_-, a minus linear combination of d_{xz} and d_{yz}. The minus combination gives a new d orbital (d_-) whose maximum amplitudes match favorably with the p orbital on C_α. As a result of orbital interactions, the metal d_+ orbital, which is the plus combination of d_{xz} and d_{yz}, remains approximately nonbonding. For an 18-electron complex, the d_+ orbital becomes the highest occupied orbital (HOMO). The bonding orbitals derived from the $a_1-\pi$ and $d_{xy}-\pi^*$ interactions constitute the two metal$-(\eta^2$-alkenyl) σ bonding orbitals ($M-C_\alpha$ and $M-C_\beta$) while the d_--p bonding orbital is the metal$-(\eta^2$-alkenyl) π bonding orbital ($M{=}C_\alpha$) in the metallacyclopropene unit. Figure 3 shows the spatial plots[21] of the three highest occupied molecular orbitals calculated for $[Re(Cl)(PH_3)_4(\eta^2\text{-}CHCH_2)]^+$ **2**, giving support to the orbital interaction argument here. A qualitative orbital interaction diagram similar to Figure 2 was also proposed previously by Templeton and co-workers.[14]

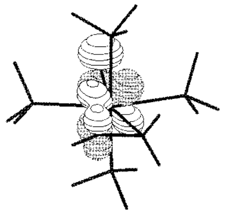
Analogous $ML_5(\eta^2$-alkene) Complexes. Before we continue our discussion on the metal η^2-alkenyl complexes, let us examine whether there is a similar structural preference in analogous $ML_5(\eta^2$-alkene) complexes. The η^2-alkene-to-metal interactions can be conveniently described by the widely used Dewar$-$Chatt$-$Duncanson model.[22] The metal$-(\eta^2$-alkene) σ bonding involves the alkene's π electron donation to the ML_5's a_1 frontier orbital. The alkene's π^* orbital interacts with one of the ML_5's "t_{2g}" set orbitals. These two types of interactions resemble those in the metal$-(\eta^2$-alkenyl) case (Figure 2). The alkene ligand, however, does not have the additional p orbital (as the η^2-alkenyl ligand has), which allows $M{=}C_\alpha$ π bonding.



d_+ ("$d_{xz}+d_{yz}$")
The highest occupied
molecular orbital



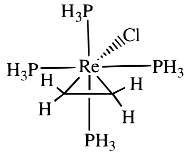
d_{xy}-π^*
Metal(d)-η^2-alkenyl(π^*)
back-donation



d-p
$Re{=}C_\alpha$ π-bonding

Figure 3. Spatial plots of the three highest occupied molecular orbitals of $[Re(Cl)(PH_3)_4(\eta^2\text{-}CHCH_2)]^+$ **2** obtained from the B3LYP calculations.

The model complex $[Re(Cl)(PH_3)_4(\eta^2\text{-}H_2C{=}CH_2)]$ **3** was used to study the energetics of η^2-alkene rotation.



3

The potential energy surface corresponding to the rotation is shown in Figure 4. The surface shows four degenerate minima corresponding to conformations in which the C$-$C vector is parallel to one of the $H_3P-Re-PH_3$ axes. The rotational barrier is 2.9 kcal/mol. The result of these calculations indicates that the analogous $ML_5(\eta^2$-alkene) complex also has a structural preference

---

[21] The spatial drawing of MO orbitals was plotted with Molden v3.3 program. The Molden package was written by G. Schaftenaar, CAOS/CAMM Center Nijmegen, Toernooiveld, Nijmegen, The Netherlands, 1997.

[22] (a) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939. (b) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71.

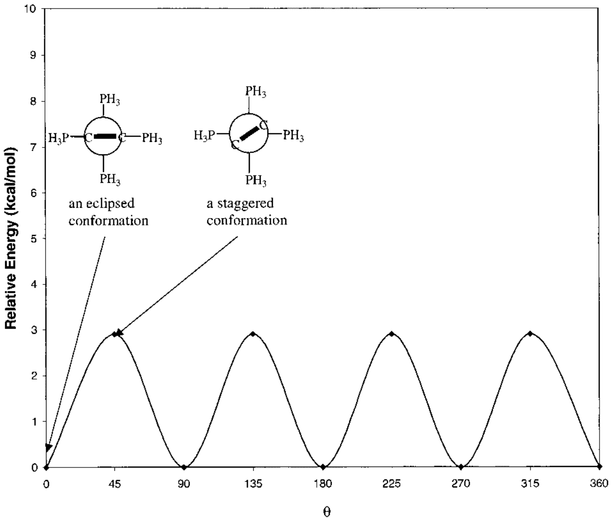
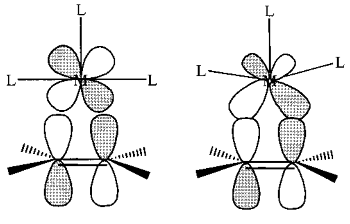


Figure 4. Potential energy surface for **3** showing the change in relative energy with respect to θ (deg).

for an eclipsed conformation ($\theta = 0°$) over a staggered conformation ($\theta = 45°$). A number of $ML_5(\eta^2$-alkene) complexes which do not contain a Cp ligand can be found in the literature. These complexes indeed show the structural preference for a dihedral angle θ being close to 0°. For example, $[ReCl(\eta^2\text{-}H_2CC{=}CHPh)(Ph_2PC_2H_4PPh_2)_2]$[23] has a dihedral angle θ of 2.6° and $Li_2\{MnH(\eta^2\text{-}H_2C{=}CH_2)[CH_2(Me)PC_2H_4PMe_2]_2\}$[24] has an angle of 5.3°.

What is the origin of this structural preference in the $ML_5-(\eta^2$-alkene) complexes? Examining the structural details of the optimized model complex **3**, we found that the eclipsed conformation ($\theta = 0°$) has shorter Re−C bond lengths (2.214 Å) than the staggered conformation ($\theta = 45°$) (2.242 Å). The NBO analysis consistently shows stronger Re−C bonds for the eclipsed conformation with a Wiberg bond index of 0.560 (0.545 for the staggered conformation). These results are consistent with the notion that the eclipsed conformation has stronger metal−(η^2-alkene) interactions and, consequently, is more stable.

A reasonable explanation for the stronger metal−(η^2-alkene) interactions in the eclipsed conformation can be summarized as follows. When the C−C vector of the η^2-alkene ligand eclipses one of the two $H_3P-Re-PH_3$ axes, the metal−(η^2-alkene) interactions push away the two eclipsed $Re-PH_3$ bonds. The bending of the eclipsed $H_3P-Re-PH_3$ unit in turn allows the mixing of a metal p orbital with d_{xy}, shown in **4**. Such a mixing increases the $d_{xy}-\pi^*$ back-donation interaction in the metal−(η^2-alkene) unit. In other words, more favorable back-bonding to π^* is expected for an eclipsed conformation.[25] When the C−C vector is in a staggered arrangement, the bending is limited. Therefore, weaker metal−(η^2-alkene) interactions are expected. The results of calculations indeed show that the $H_3P-Re-PH_3$ angle eclipsed by the C−C vector in the eclipsed conformation is smaller (157.2°). The $H_3P-Re-PH_3$ angles in the staggered conformation are larger (165.4°).



4

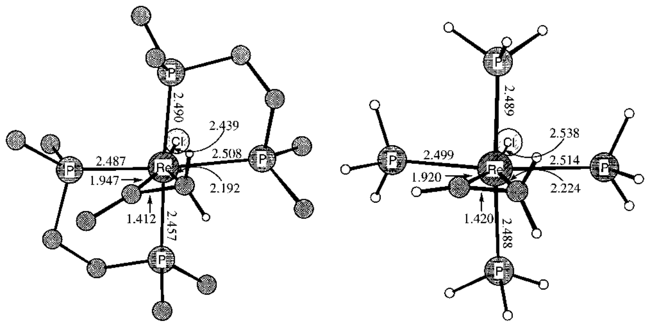


Figure 5. Observed and calculated bond lengths (Å) for $Re(Cl)[PPh_2(CH_2)_2PPh_2]_2[\eta^2\text{-}C(CH_2Ph)CH_2]\}^+$ (the CH_2Ph group on C_α is substituted by one atom for clarity) and its model complex **2**.

The mixing of metal p orbitals with d orbitals is commonly employed to explain the enhancement of metal(d)-to-ligand(π^*) back-donation.[26] The NBO analysis on the model complex $[Re(Cl)(PH_3)_4(\eta^2\text{- }H_2C{=}CH_2)]$ **3** supports the mixing argument above. The result of the analysis shows that involvement of Re p orbitals in a Re−C bond is 9.2% in the eclipsed conformation. The involvement, however, decreases to only 0.06% in the staggered conformation.

In summary, $ML_5(\eta^2$-alkene) complexes prefer to adopt a structure in which the C−C vector of the η^2-alkene ligand eclipses (is coplanar with) one of the M−L bonds. In such an arrangement, the L−M−L unit eclipsed by the C−C vector of η^2-alkene bends away from the η^2-alkene ligand. This bending allows the mixing of p orbital with d_{xy}, in turn enhances the $d_{xy}-\pi^*$ bonding, and maximizes the metal−(η^2-alkene) interactions.

$ML_5(\eta^2$-alkenyl) Complexes. The model complex $[Re(Cl)(PH_3)_4(\eta^2\text{-}CHCH_2)]^+$ **2** was used to study the energetics of η^2-alkenyl rotation. The optimized geometry of **2** together with the experimentally observed structure of $\{Re(Cl)(PPh_2C_2H_4PPh_2)_2[\eta^2\text{-}C(CH_2Ph)CH_2]\}^{+}$[12] is shown in Figure 5. The agreement between the calculated and experimental geometries is remarkably good.

The potential energy surface corresponding to the η^2-alkenyl rotation of **2** is shown in Figure 6. Surprisingly, the potential energy curve, shown in Figure 6, is very similar to that obtained for the analogous $ML_5(\eta^2$-alkene) case (Figure 4) and shows that the $C_\alpha-C_\beta$ vector of the η^2-alkenyl ligand prefers to eclipse one of the two $H_3P-Re-PH_3$ axes when $\theta = 0°$, 90°, 180°, or 270°. The barrier to rotation is 3.7 kcal/mol, only slightly higher

---

[23] Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1984**, 992.

[24] Girolami, G. S.; Howard, C. G.; Wilkinson, G.; Dawes, H. M.; Thornton-Pett, M.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 921.

[25] Butts, M. D.; Bryan, J. C.; Luo, X.-L.; Kubas, G. J. *Inorg. Chem.* **1997**, *36*, 3341.

[26] (a) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 322.

Table 2. NBO Analyses for the Model Complex [Re(Cl)(PH$_3$)$_2$(η^2-CHCH$_2$)] 2

	eclipsed conformation ($\theta = 0°$)			staggered conformation ($\theta = 45°$)		
	Re=C$_\alpha$	Re−C$_\beta$	C$_\alpha$−C$_\beta$	Re=C$_\alpha$	Re−C$_\beta$	C$_\alpha$−C$_\beta$
occupancy	1.565 (σ) 1.927 (π)	1.504	1.975	1.893 (σ) 1.936 (π)	1.780	1.979
NBO energy	−0.256 (σ) −0.404 (π)	−0.087	−0.783	−0.629 (σ) −0.401 (π)	−0.423	−0.792
Wiberg bond index	1.323	0.589	1.251	1.320	0.581	1.263
bond length (Å)	1.920	2.224	1.420	1.922	2.271	1.417

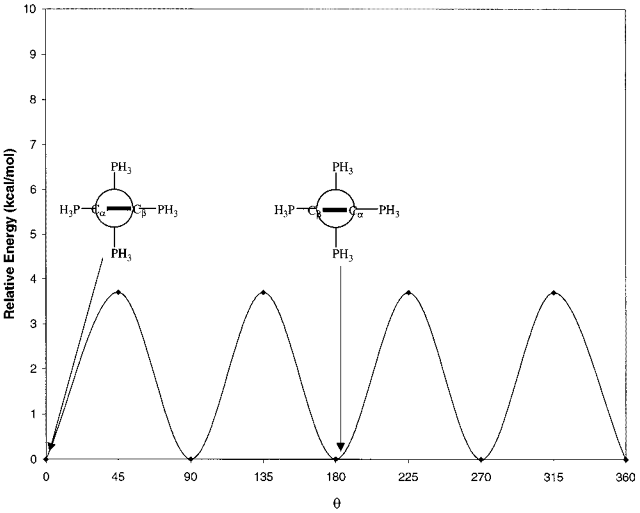


Figure 6. Potential energy surface for **2** showing the change in relative energy with respect to θ (deg).

than that for the η^2-alkene analogue. The prediction of structural preference is consistent with the experimental observation (see Table 1).

The discussion above shows that both ML$_5$(η^2-alkene) and ML$_5$(η^2-alkenyl) complexes involve the Dewar−Chatt−Duncanson type of interactions, i.e., the a$_1$−π and d$_{xy}$−π^* bonding interactions. The η^2-alkenyl complex, however, possesses an additional d−p π bonding interaction which constitutes the M=C$_\alpha$ π bonding. The similarity between the two potential energy curves for the η^2-alkenyl and η^2-alkene complexes suggests that the additional M=C$_\alpha$ π bonding does not change the structural preference. In other words, the M=C$_\alpha$ π bonding interaction likely remains the same upon the η^2-alkenyl rotation and the orientation of the η^2-alkenyl ligand in these η^2-alkenyl complexes, ML$_5$(η^2-alkenyl), is thus determined only by the d$_{xy}$−π^* interaction as the case in ML$_5$(η^2-alkene) complexes. The importance of the d$_{xy}$−π^* back-donation interaction in determining the stability of η^2-alkenyl complexes was emphasized previously, although no calculation was made.[10]

Detailed NBO analyses (Table 2) show that the occupancies and energies change drastically from the eclipsed ($\theta = 0°$) to the staggered ($\theta = 45°$) conformation for the Re−C$_\alpha$ and Re−C$_\beta$ σ bonds. For the Re=C$_\alpha$ π bond, the changes in the occupancies and energies, however, are not significant. These results further support the conclusion that the strength of Re=C$_\alpha$ π bonding does not change much upon the η^2-alkenyl rotation.

The preference for an eclipsed conformation is again related to the better d$_{xy}$−π^* back-donation interaction, a result of more metal p orbital involvement in the Re−C σ bonds for the preferred structure. For the eclipsed ($\theta = 0°$) conformation, the metal p orbital characters in the Re=C$_\alpha$ and Re−C$_\beta$ bonds are 10% and 22%, respectively. The corresponding metal p orbital characters decrease to less than 1% for the staggered conformation ($\theta = 45°$).

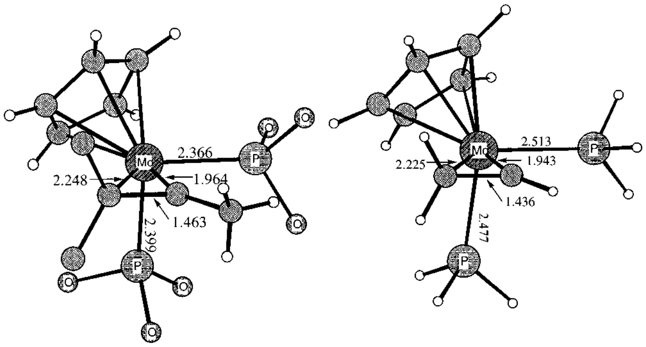


Figure 7. Observed and calculated bond lengths (Å) for [CpMo[P(OMe)$_3$]$_2$(η^2-CMeCPh$_2$)] (the two phenyl groups on C$_\beta$ are substituted by two atoms for clarity) and its model complex [CpMo(PH$_3$)$_2$(η^2-CHCH$_2$)].

MCpL$_2$(η^2-alkenyl) Complexes. Transition-metal η^2-alkenyl complexes containing a Cp ligand also tend to adopt conformations in which the η^2-alkenyl ligand eclipses one of the M−L bonds, i.e., the dihedral angle θ is close to 0° or 180°. The model complex [CpMo(PH$_3$)$_2$(η^2-CHCH$_2$)] was used to study the energetics of the η^2-alkenyl rotation. The optimized geometry along with the experimentally observed structure of [CpMo[P(OMe)$_3$]$_2$(η^2-CMeCPh$_2$)][6] is shown in Figure 7. The agreement between the calculated and experimental structural parameters is relatively good.

The potential energy curve corresponding to the η^2-alkenyl rotation in the model complex is shown in Figure 8. The conformations with $\theta = 90°$ and 180° are the most stable enantiomeric pair (see Figure 1b for the enantiomeric relationship). Although the conformations with $\theta = 0°$ and 270° (also an enantiomeric pair) do not correspond to energy minima in the potential energy curve, they occur in the region of low energies. A special feature of the potential energy curve is that the surface is very flat from $\theta = 270°$ to 360° (0°) (see Figure 8). Conformations corresponding to the flat region are only about 2.5 kcal/mol higher in energy than the most stable conformation. These results indicate that conformations in which the η^2-alkenyl ligand eclipses one of the M−L bonds together with those in the region from $\theta = 270°$ to 360° are all possible, in an agreement with the experimental observation (Table 1). To further confirm the observed feature in the calculated potential energy curve, we also did calculations on other model complexes, [CpRe(PH$_3$)$_2$(η^2-CHCH$_2$)]$^+$ and [CpW(CO)$_2$(η^2-CHCH$_2$)]. The potential energy curves obtained for these model complexes are very similar to the one shown in Figure 8.

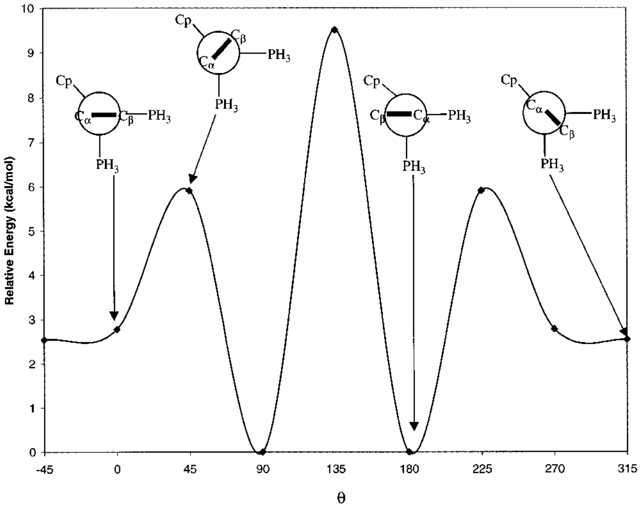


Figure 8. Potential energy surface for model complex [CpMo(PH$_3$)$_2$(η^2-CHCH$_2$)] showing the change in relative energy with respect to θ (deg).

Conformations in which the C$_\alpha$−C$_\beta$ vector of the η^2-alkenyl ligand eclipses one of the M−L bonds correspond to either energy minima or low energies in the potential energy curve. This feature suggests that the electronic reason for the change in the structural preference discussed for ML$_5$(η^2-alkenyl) complexes should also be applicable to the case for η^2-alkenyl complexes containing a Cp ligand. The applicability can be understood because a Cp ligand can be considered as a tridentate ligand and MCpL$_2$ is isolobal with the ML$_5$ fragment.[27] The conformation with $\theta = 135°$ has a particularly high energy. On the contrary, conformations in the region of $\theta = 270°$ to 360° have lower energies and their stabilities are similar. These results, however, suggest that the steric effect of the bulky Cp ligand is also operative. When $\theta = 135°$, the C$_\alpha$−C$_\beta$ vector is expected to have the greatest steric repulsive interaction with the Cp ligand (see Figure 8 for the relative orientation of the C$_\alpha$−C$_\beta$ vector). When θ is in the region from 270° to 360°, the C$_\alpha$−C$_\beta$ unit can be considered as in a trans arrangement with respect to the Cp ligand. In summary, the orientation of η^2-alkenyl ligand in transition-metal η^2-alkenyl complexes is governed by both electronic and steric factors.

Conclusion

The preference for coplanarity of the η^2-alkenyl and one of the metal−ligand bonds in transition-metal η^2-alkenyl complexes has been examined with the aid of density functional molecular orbital calculations and simple orbital interaction models. The metal−η^2-alkenyl bonding in these complexes involves the Dewar−Chatt−Duncanson type of interactions (the donation of η^2-alkenyl π electrons to the metal center and the metal(d)−η^2-alkenyl(π*) back-donation) and metal(d)−C$_\alpha$(p) π bonding. Density functional theory calculations suggest that the Dewar−Chatt−Duncanson type of interactions determines the structural preference observed experimentally for a variety of η^2-alkenyl complexes. When the C$_\alpha$−C$_\beta$ vector of the η^2-alkenyl ligand eclipses (is coplanar with) one of metal−ligand bonds, the metal−η^2-alkenyl interactions are the strongest because the mixing of metal p orbitals with d orbital, resulting from the metal−ligand distortion, enhances the metal(d)−η^2-alkenyl(π*) back-donation. The metal−C$_\alpha$ π bonding is found to play a small role in determining the preferred orientation of the η^2-alkenyl ligand. For η^2-alkenyl complexes containing a Cp ligand, the steric effect of the bulky Cp ligand is also operative, although the electronic factors described above are still dominant in determining the structural preference.

Acknowledgment. This work was supported by the Research Grants Council of Hong Kong and the Hong Kong University of Science and Technology.

OM990024I

---

[27] (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 381.