Metal Carbene or Carbenoid Complexes? A Theoretical Study of the Active Form of Transition Metal Catalysts in Cyclopropanation and Olefin Metathesis Reactions

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Summary: We have carried out a theoretical investigation at the DFT level on the active form of the catalyst of cyclopropanation and olefin metathesis reactions catalyzed by transition metals. These species can exist as metal carbene complexes $L_nM{=}CR_2$ *or carbenoid complexes* $L_{n-1}M{-}CR_2{-}L$ *(L = ligand). We have considered the cases M = Ru, Rh, Pd, and Zn, and we have found that the preferred form depends on the nature of the metal. A diabatic model has been used to rationalize these computational results.*

Introduction

Metal carbene complexes of the general form

$$[L_nM{=}CR_2 \leftrightarrow L_nM^{-}{-}C^{+}R_2]$$

have been proposed as the active species in cyclopropanation and olefin metathesis reactions[1] catalyzed by transition metals. These species, which are usually obtained from the catalytic decomposition of diazocompounds by transition metal complexes, contain a carbene unit which, for instance, can be transferred to an olefin substrate to afford the cyclopropane product.

A number of experimental results support this structural hypothesis: various ruthenium alkylidene species of the type $(PR_3)_2Cl_2Ru{=}CHR'$ have been isolated by Schwab and co-workers[2] and Grunwald and co-workers.[3] Some of these compounds have also been characterized by X-ray crystal structure analyses. $(PCy_3)_2Cl_2Ru{=}CH\text{-}p\text{-}C_6H_4Cl$, for instance, has been demonstrated to exist in a distorted square-pyramidal geometry where the two phosphine ligands are trans to each other and the alkylidene unit lies in the Cl−Ru−Cl plane.[2] However other experimental evidence suggests that in many cases the active species could be a carbenoid derivative similar to that proposed for the Simmons−Smith cyclopropanation reaction in various experimental[4] and theoretical[5] investigations. This carbenoid species can be considered to be the insertion product that is obtained by decomposition of diazocompounds in the presence of transition metal derivatives (eq 1).

$$L_n{-}M{-}X + RR'CN_2 \rightarrow L_n{-}M\text{-}CRR'{-}X + N_2\ (L = \text{ligand},\ X = \text{halogen}) \quad (1)$$

Insertion reactions of this type have been reported for M−H, M−N, and M−halogen (halogen = Cl, Br, I) bonds with simple diazocompounds. Quite recently McCrindle and co-workers isolated α-halogenomethyl derivatives of palladium and platinum, and for the two complexes $(PPh_3)_2Pd(CH_2Cl)Cl$ and $(PPh_3)_2Pt(CH_2Cl)Cl$ they have studied in detail the X-ray structures.[6]

Since a knowledge of the structure of the active species is essential to understand the mechanism of cyclopropanation and olefin metathesis, we have performed a theoretical study using a density functional theory (DFT) approach[7] and a diabatic analysis of the carbene and carbenoid species involving ruthenium, rhodium, palladium, and zinc, which are transition metals commonly used in this type of catalyzed reactions. We have chosen as a model system for the catalyst the species Cl_2MCH_2 with M = Ru, Rh, Pd, Zn, and in all cases we have computed the energy profile along the coordinate that connects the metal carbene structure to the carbenoid structure. To check the reliability of this simple model, we have also investigated the species $Cl_2(PR_3)_2MCH_2$ (R = H, Me), which better emulates the real catalyst employed in the experiment.

Computational Procedure

All the DFT computations have been performed with the Gaussian 98 series of programs[8] using the hybrid Becke's three-parameter exchange functional denoted as B3LYP[9] and the DZVP basis set.[10] The geometry of the various carbene and

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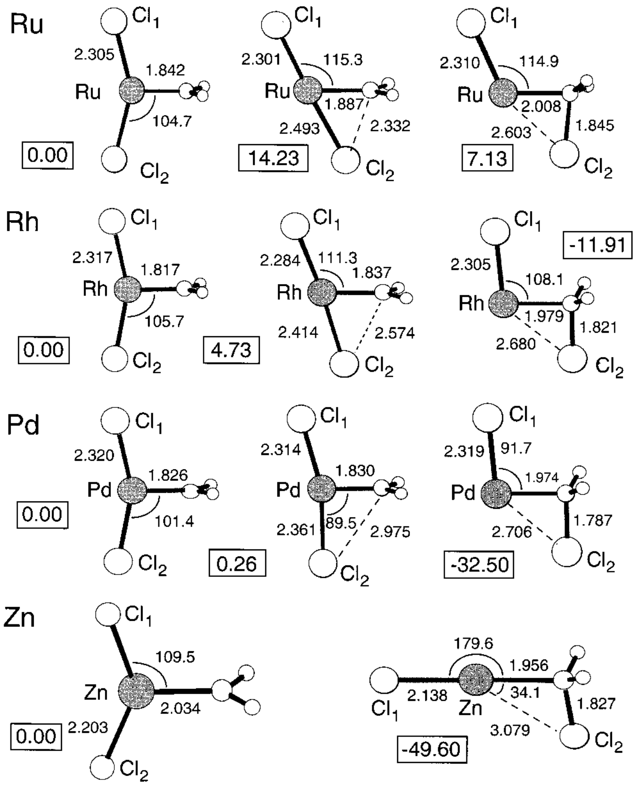

Figure 1. Schematic representation of the metal carbene and carbenoid structures and of the transition state connecting the two forms for the model system Cl_2MCH_2, M = Ru, Rh, Pd, Zn. The values of the relative energies (kcal mol^{-1}) and those of the most relevant geometrical parameters (angstroms and degrees) are reported.

carbenoid structures has been fully optimized with the gradient method available in Gaussian 98, and in all cases a frequency computation has been carried out on the optimized structures.

Results and Discussion.

A. Cl_2MCH_2 Model System. All the computed structures for M = Ru, Rh, Pd, and Zn are schematically represented in Figure 1. In the figure we have reported the values of the most relevant geometrical parameters and the relative energies of the metal carbene and carbenoid species and of the transition state connecting the two forms. The computational results can be summarized as folllows.

(i) The ground-state for Cl_2ZnCH_2 and Cl_2PdCH_2 is a singlet, while Cl_2RhCH_2 and Cl_2RuCH_2 exist as doublet and triplet ground states, respectively.

(ii) For the three cases involving palladium, rhodium, and ruthenium we have located both the carbene and carbenoid species. While for palladium and rhodium the carbenoid form is more stable than the metal carbene form by 32.50 and 11.91 kcal mol^{-1}, respectively, for ruthenium the metal carbene becomes preferred by 7.13 kcal mol^{-1}.

(iii) The transition state connecting the two forms involves a migration of one chlorine atom (Cl_2 in Figure 1) from the metal to the carbon in the Cl_1−M−C plane. The transition state becomes more and more similar to the carbenoid structure in the direction Pd → Rh → Ru (the C−Cl_2 bond length is 2.975, 2.574, and 2.332 Å for Pd, Rh, and Ru, respectively).

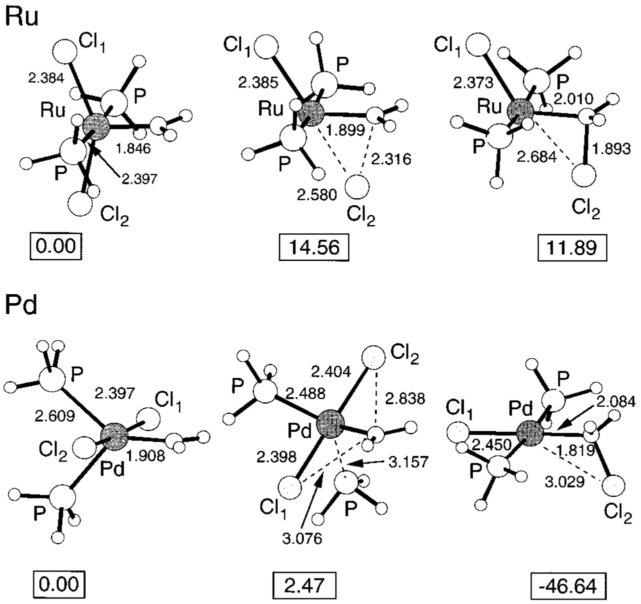

Figure 2. Schematic representation of the metal carbene and carbenoid structures and of the transition state connecting the two forms for the model system $Cl_2(PH_3)_2MCH_2$, M = Ru, Pd. The values of the relative energies (kcal mol^{-1}) and those of the most relevant geometrical parameters (angstroms and degrees) are reported.

(iv) The barrier that must be overcome to transform the metal carbene structure to the carbenoid structure increases in the direction Pd → Rh → Ru.

(v) The species involving zinc only exists as a carbenoid form. The metal carbene structure corresponds to a transition state connecting two equivalent carbenoid forms, as proved by the frequency computation.

B. $Cl_2(PH_3)_2MCH_2$ and the $Cl_2(PMe_3)_2MCH_2$ Model Systems. The computational data obtained for the Cl_2MCH_2 system seem to indicate that the preferred structural features of the catalyst (carbene or carbenoid form) depend on the nature of the metal. To verify how appropriate our simple model system is to emulate the catalyst, for the two cases M = Ru, Pd, we have investigated the more complex system $Cl_2(PH_3)_2MCH_2$, which is closer to the real catalytic species employed in the experiment. The results are schematically reported in Figure 2 and can be summarized as follows.

(vi) The ground state for both complexes ($Cl_2(PH_3)_2RuCH_2$ and $Cl_2(PH_3)_2PdCH_2$) is a singlet.

(vii) The carbene and carbenoid forms exist for both ruthenium and palladium. As previously found, the carbene form is more stable in the former case, while the carbenoid form becomes the preferred one in the latter. Also, the thermodynamics of the carbene−carbenoid equilibrium does not change dramatically with respect to the simpler Cl_2MCH_2 model; in the present case, for M = Ru the carbenoid form is 11.89 kcal mol^{-1} higher in energy than the carbene species, while for M = Pd the carbenoid becomes 46.64 kcal mol^{-1} more stable than the carbene.

(viii) The transition state geometry and the corresponding activation barriers are similar to those previously determined for the simple model. The barriers are now 14.56 kcal mol^{-1} (14.23 kcal mol^{-1} in Cl_2RuCH_2) and 2.47 kcal mol^{-1} (0.26 kcal mol^{-1} in Cl_2PdCH_2). The steric hindrance of the PH_3 ligands makes both transi-

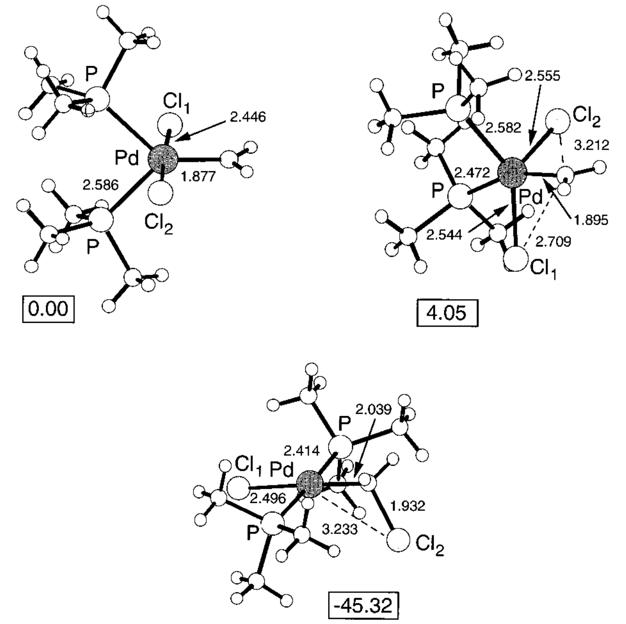

Figure 3. Schematic representation of the metal carbene and carbenoid structures and of the transition state connecting the two forms for the model system $Cl_2(PMe_3)_2PdCH_2$. The values of the relative energies (kcal mol^{-1}) and those of the most relevant geometrical parameters (angstroms and degrees) are reported.

tion states slightly more carbenoid-like: for ruthenium and palladium the new forming $C-Cl_2$ bond becomes 2.316 Å (2.332 Å in Cl_2RuCH_2) and 2.838 Å (2.975 Å in Cl_2PdCH_2), respectively.

For M = Pd we have also examined a model system where each PH_3 ligand has been replaced by a PMe_3 ligand. The $Cl_2(PMe_3)_2PdCH_2$ model[11] should better emulate the steric interactions that characterize the real catalytic systems, where bulky substituents are usually involved. From the results summarized in Figure 3, it is evident that the inclusion of more cumbersome ligands leaves almost unchanged the thermodynamics of the carbene–carbenoid equilibrium: the carbenoid form is now 45.32 kcal mol^{-1} more stable than the carbene species. Also, no relevant changes have been detected in the carbene → carbenoid activation barrier, which remains quite low, being now 4.05 kcal mol^{-1}.

C. Diabatic Model. The computational data discussed in the previous sections unambiguously show that the preferred form of the catalytic species depends on the nature of the metal. They also indicate that the thermodynamics of the carbene–carbenoid equilibrium is satisfactorily described by the simple Cl_2MCH_2 model system. We shall now use this simple model to demonstrate that the preference for the carbene or carbenoid form can be understood by considering the energies of bonds being formed and being broken on passing from one structure to the other. Also, we shall show that a simple diabatic model based upon spin recoupling in VB theory[12] can rationalize the trend of the energy barriers and the nature of the transition state.

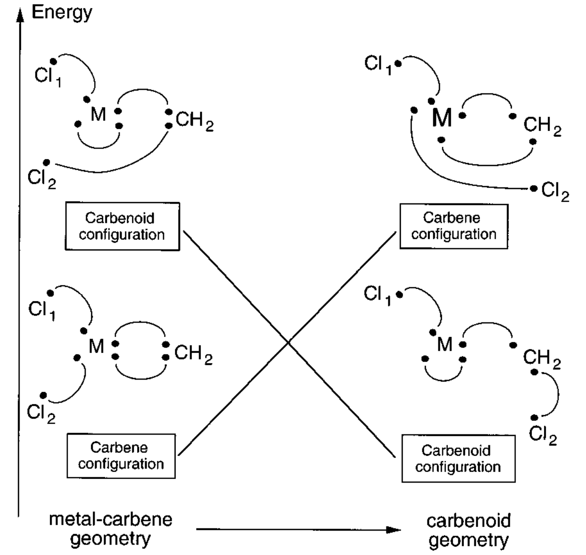

Figure 4. Carbene (left) and carbenoid (right) configurations.

To this purpose, we must consider the two electronic configurations that describe the electron-spin coupling associated with the metal carbene structure (carbene configuration) and with the carbenoid structure (carbenoid configuration), respectively. The bonds that are broken on passing from carbene to carbenoid (destabilizing effect) are the M–C π bond and the $M-Cl_2$ σ bond. The four electrons involved in these bonds are coupled again (stabilizing contribution) in the carbenoid structure to form the new σ $C-Cl_2$ bond and the metal lonepair. A schematic representation of the two configurations, at both carbene and carbenoid geometries, is given in Figure 4.

To estimate how the energy of the π M–C bond varies along the series Ru → Rh → Pd → Zn, we have considered the DFT energy of the following reaction:

$$\mathrm{Cl_2M{=}CH_2 + H^{\bullet} \rightarrow Cl_2M{-}CH_3\ (M = Ru, Rh, Pd, Zn)} \quad (2)$$

If we assume for the C–H bond energy a standard value of 104 kcal mol^{-1}, we obtain the following estimate (kcal mol^{-1}) for the trend (not the absolute value) of the various π bonds:

$$\mathrm{Ru\ (31) > Rh\ (27) > Pd\ (20) > Zn\ (0)} \quad (3)$$

Furthermore the following values of the σ $M-Cl_2$ bond energies (kcal mol^{-1}) can be used:[13]

$$\mathrm{Ru\ (92),\ Rh\ (62),\ Pd\ (42),\ Zn\ (55)} \quad (4)$$

Since the contributions associated with the formation of the $C-Cl_2$ bond and that due to the electron coupling

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[11] The geometry of the $Cl_2(PMe_3)_2PdCH_2$ complex has been fully optimized at the B3LYP level using the effective-potential LANL2DZ basis (Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270; Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284; Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299). To obtain more reliable energy values, which can be compared to those of the simpler Cl_2PdCH_2 and $Cl_2(PH_3)_2PdCH_2$ systems, single-point computations have been carried out with the more accurate DZVP basis [10] on the LANL2DZ optimized structures.

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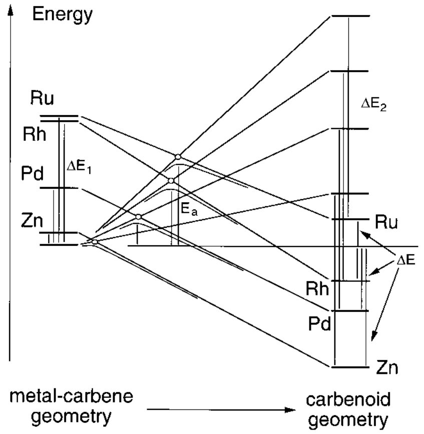

Figure 5. Diabatic diagram corresponding to the metal carbene structure → carbenoid structure transformation for M = Ru, Rh, Pd, Zn.

to form the metal lone-pair can be reasonably assumed to be roughly constant along the series Ru, Rh, Pd, and Zn, the trend of the energies of the π M−C bond and of the M−Cl_2 bond explains the computed trend of the energy difference between the carbene and carbenoid form.

The carbene and carbenoid configurations are now used, within a diabatic model, as basis functions to represent, as a linear combination, the total wave function of the system at any point along the coordinate that connects the carbene to carbenoid. On going from carbene to carbenoid, the energy of the carbene configuration increases and that of the carbenoid configuration decreases as schematically indicated in Figure 4. This process can be more satisfactorily represented in a diagram where we report the total energy of the system versus the coordinate connecting the two structures. This energy profile is broken down into two component curves which describe the energy behavior of the carbene configuration (carbene diabatic) and of the carbenoid configuration (carbenoid diabatic). The crossing between the two diabatic curves determines the position of the transition state and the magnitude of the activation energy.

The qualitative trends of the repulsive carbene diabatic and of the attractive carbenoid diabatic for M = Ru, Rh, Pd, and Zn are represented in Figure 5, where the left side of the diagram corresponds to the metal carbene geometry and the right side of the diagram to the carbenoid geometry. In this diagram the position of the crossing and the size of the barrier depend on three factors: (1) the energy difference ΔE between the carbenoid structure and the metal carbene structure; (2) the energy difference ΔE_1 between the carbene and carbenoid diabatic at the metal carbene geometry (left side of the diagram); (3) the energy difference ΔE_2 between the carbene and carbenoid diabatic at the carbenoid geometry (right side of the diagram). ΔE corresponds to the computed quantomechanical energies (reported in Figure 1), whose trend has been previously rationalized in terms of bond energies. ΔE_1 is approximately determined by the algebraic sum of three contributions: (a) the energies required for decoupling the two electrons of the π component of the M−C bond; (b) the energy needed for decoupling the two electrons of the σ M−Cl_2 bond; (c) the energy obtained after coupling the two electrons of the metal lone-pair. We can reasonably assume that the coupling of the remaining two electrons is energetically negligible since these electrons are too far away. Since the two contributions (a) and (b) can be approximately evaluated from the energies of the corresponding bonds (previously discussed) and the contribution associated with the formation of the metal lone-pair has been assumed to be roughly constant for the various metals, the sum of (a) and (b) determines the following trend of ΔE_1:

$$\mathrm{Ru} > \mathrm{Rh} > \mathrm{Pd} > \mathrm{Zn}$$

The trend of ΔE_2 can be evaluated in a similar way. The magnitude of this term is determined by (d) the energy required for decoupling the two electrons of the C−Cl_2 bond and the two electrons of the metal lone-pair and (e) the energy obtained after coupling the two π electrons of the M−C bond. Since the contribution (d) can again be assumed to be roughly constant along the series Ru, Rh, Pd, and Zn, the trend of ΔE_2 is the same as that of the π M−C bond, i.e., Ru > Rh > Pd > Zn.

In conclusion the previous discussion provides the following information of chemical interest.

(A) All three factors ΔE, ΔE_1, and ΔE_2 are simultaneously responsible for the decreasing of the metal carbene → carbenoid barrier in the direction Pd → Rh → Ru and for the increasing carbenoid character of the transition state in the same direction, as shown in Figure 5.

(B) The two factors that determine the preferred form of the catalyst are the energies of the π M−C bond and the σ M-Cl_2 bond: the larger the energies of these two bonds, the more stable the carbene structure becomes. The case of the Ru complex illustrates a situation where these two bonds are strong enough to make the metal carbene the preferred form. The opposite situation is represented by the zinc complex, where these two bonds are too weak and the metal carbene structure is converted to a transition state.

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