Theoretical studies of inorganic and organometallic reaction mechanisms. 8. Hydrogen exchange in the β-agostic ethylene complex of cyclopentadienyl rhodium

Zhenyang Lin and Michael B. Hall

Department of Chemistry, Texas A&M University, College Station, TX 77843 (USA)

Martyn F. Guest * and Paul Sherwood

SERC Daresbury Laboratory, Warrington, WA4 4AD (UK)

Abstract

Ab initio calculations with effective core potentials have been used to study the hydrogen exchange processes of the $[CpRh(C_2H_4)(\eta^2\text{-}C_2H_5)]^+$ β-agostic complex. The mirror-symmetric olefin–hydride species is found to be an intermediate (3.4 kcal mol^{-1} higher in energy than the β-agostic complex) rather than a transition state (≈ 5 kcal mol^{-1}) in the interconversion process of the two enantiomeric forms. A higher energy process involving rotation of the methyl group in the agostic complex is determined to occur through an Rh $\cdots (\eta^2\text{-}H_2C)$ interaction with a calculated activation energy of ≈ 6.5 kcal mol^{-1}. Complete loss of the Rh $\cdots$ H–C agostic interaction requires an activation energy of about 14 kcal mol^{-1}. This agostic interaction's strength depends upon the M $\cdots$ H overlap, and stronger agostic interactions result in weaker C–H$_{agostic}$ bonds. An even higher energy process involving the exchange of all of the nine hydrogens and the four carbons is found to be due to the ethylene rotation in the agostic complex. The ethylene rotation barrier (calculated to be 9.8 kcal mol^{-1}) depends greatly on the sizes of the transition metal atom and ligands in the complex since steric effects play an important role in the rotation.

*Key words:* Ab initio calculations; Agostic interactions; Hydrides; Rhodium

1. Introduction

Complexes containing "agostic" C–H $\cdots$ M interactions have attracted considerable interest since they serve as models for the initial step in C–H activation [1]. In addition, some agostic ethyl species are important catalysts in metal-catalyzed olefin polymerization reactions [2,3]. Recently, NMR spectroscopic studies have established that several Rh and Co agostic ethyl species **1** are in rapid equilibrium with the terminal hydride species **2** [4]. By NMR spectroscopy, the lowest energy process, which has a ΔG value < 7 kcal mol^{-1} for both Co and Rh complexes, involves an equilibrium between a β-agostic complex (**1**) and a terminal hydride (**2**, also called olefin–hydride) (see Scheme 1). In this process, the olefin-hydride complex could be either

an intermediate or a transition state. For the Rh complex, two other higher energy processes were detected by ^{1}H and ^{13}C NMR spectroscopy. The first one, with $\Delta G = 8.5$ kcal mol^{-1}, involves the rotation of an agostic methyl group. This rotation could occur by loss of the agostic interaction and rotation of the methyl group in a 16-electron intermediate [4b] or it could occur by simultaneous formation of a new M $\cdots$ H–C agostic interaction as the first one breaks through an M $\cdots (\eta^2\text{-}H_2C)$ interaction. The final process, which ultimately exchanges all nine hydrogens and the four carbons, has $\Delta G = 9.6$ kcal mol^{-1}. The mechanism of this last process must involve either ethylene rotation or inversion at the metal center (see Scheme 2), but which mechanism is operable cannot be determined from the variable temperature NMR [4].

Molecular orbital methods have been widely and successfully used to elucidate inorganic and organometallic reaction mechanisms [5,6]. In this paper ab initio quantum chemical calculations are used to study

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Correspondence to: Professor M.B. Hall.
* Present address: Pacific Northwest Laboratory, P.O. Box 999, Richland, WA99352, USA.
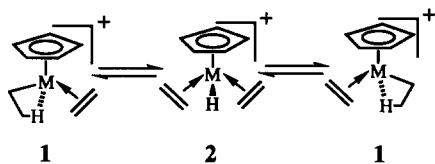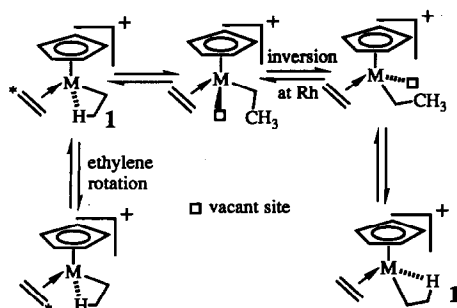
Scheme 1.

the reaction mechanisms discussed above, and to determine the intermediate, transition state and reaction paths which cannot be resolved experimentally. The nature of the agostic interaction is also discussed.

2. Theoretical details

Effective core potentials [7] were employed in all ab initio calculations. All geometries were optimized at second-order Møller–Plesset (MP2) levels [8]. In this study, the C_5H_5 unit was fixed as planar with C–C and C–H bond lengths of 1.41 Å and 1.08 Å, respectively.

In the effective core potentials (ECPs) for the rhodium atom, the outermost core orbitals, which correspond to a ns^2np^6 configuration, were treated explicitly along with the nd, $(n + 1)$s and $(n + 1)$p valence orbitals [7a]. The ECP basis sets of the Rh atom were described with double-ζ representations for the 5s/4p/4d electrons, (541/41/21) [7a]. For ligand atoms, the ECPs and double-ζ basis sets of Stevens et al. were used [7b], where [He] and [Ne] configurations were taken as cores for the first and second row main group atoms, respectively. The Dunning–Huzinaga double-ζ basis set (31) was used for the hydrogen atom [9].

The MP2 geometry optimizations are necessary because the restricted Hartree–Fock (RHF) calculations give poor results for both the geometry and the energy. For example, the Rh–ethylene distance in the β-agostic [CpRh(C_2H_4)(C_2H_5)]$^+$ complex (1) was calculated to be 2.46 Å at the RHF level, while MP2 calculation gave 2.10 Å (in CpRh(C_2H_4)(C_2F_4) complex, the experimental value of the Rh-ethylene distance is 2.06 Å [10]). At RHF level, the calculated activation energy is 10.3 kcal mol^{-1} for the interconversion process between the two enantiomeric forms of the [CpRh-

Scheme 2.

(C_2H_4)(C_2H_5)]$^+$ complex (see Scheme 1). This calculated activation energy (RHF) is too large when compared to the experimental result.

It should also be noted here that only reaction energies computed at the MP2 level (ΔE) without zero-point energy corrections were calculated and these ΔE values were compared with experimentally measured reaction free energies (ΔG). These comparisons should be reasonable since the contributions from entropy changes are relatively small because only structural rearrangements within a molecule are involved in the considered reaction process (see Schemes 1 and 2). Since several structures are not fully optimized, zero-point energy corrections have not been made. These corrections are expected to be about 2 kcal mol^{-1}.

All ab initio calculations were performed with the GAMESS and Gaussian 92 software [11], at the Cornell National Supercomputer Facility (CNSF) on an IBM RISC Systems/6000, and at the Supercomputer Center of Cray Research, Inc., Minnesota on a Cray Y-MP8I/8128-2. The laplacian of valence electron density was plotted with the use of the MOPLOT program [12].

3. Results

3.1. Equilibrium between the β-agostic complex and olefin–hydride

To define the equilibrium process shown in Scheme 1, we began by optimizing the olefin–hydride complex (2) within C_s symmetry. Figure 1(C) shows the resulting optimized structure. To obtain the structure of the β-agostic complex (1), we fixed the Rh–Cp bond length and one of the two C_2H_4 units from the optimized olefin–hydride, and then optimized all other structural parameters. Figure 1(A) shows the optimized structure of the β-agostic complex. In the β-agostic complex (see 1 and Fig. 1(A)), the agostic C–H bond (1.20 Å) is significantly longer than a normal C–H bond (1.08 Å), and there is a short Rh $\cdots$ H contact (1.87 Å), which indicates significant Rh $\cdots$ H–C interaction. In contrast, the Rh-H distance is 1.57 Å in the olefin-hydride complex (see 2 and Fig. 1(C)). Energetically, the olefin–hydride is 3.4 kcal mol^{-1} less stable than the β-agostic complex (see Fig. 1).

To determine whether the olefin-hydride is an intermediate or a transition state, we could calculate the complete reaction path for the hydrogen transfer from the olefin-hydride to the β-agostic complex. To avoid this high computational effort, we chose a more economical way of resolving this one question by optimizing a structure with the Rh $\cdots$ H and C $\cdots$ H distances constrained to be equal (see Fig. 1(B)). This constrained "halfway" structure is not expected to be far from the true reaction profile in the potential
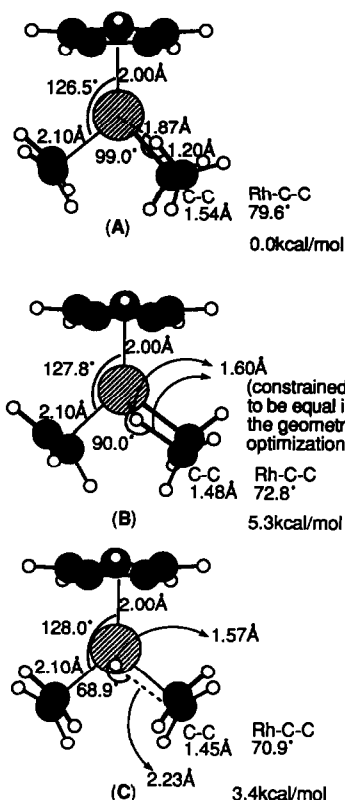
Fig. 1. Optimized structures of the β-agostic complex, [CpRh-$(C_2H_4)(\eta^2$-$C_2H_5)]^+$, (A); an approximate transition state (B); and the olefin–hydride isomer (C).

surface because the Rh ··· H (1.72 Å) and C ··· H (1.715 Å) distances are nearly equal in the average geometry of the β-agostic complex (Fig. 1(A)) and its olefin–hydride isomer (Fig. 1(C)). If this "halfway" structure is higher in energy than the olefin–hydride, we can be sure that the olefin–hydride is an intermediate. The result shows that this "halfway" structure is 1.9 kcal mol⁻¹ higher in energy than the olefin–hydride and 5.3 kcal mol⁻¹ higher in energy than the β-agostic complex. If this "halfway" structure is approximately taken as a transition state of the interconversion process between the β-agostic complex and the olefin–hydride, the activation energy is about 5 kcal mol⁻¹, a value which is in good agreement with the experimental result. Chart 1 shows the energy profile of Scheme 1.

3.2. Rotation of the methyl group in the β-agostic complex

If a new M ··· H–C agostic bond forms as the first one breaks, the system passes through an M ··· (η^2-H_2C) structure. To examine this process, we began with the β-agostic complex (see Fig. 2(A)), rotated the methyl group along the C–C bond by 60°, fixed the methyl group at this orientation, and then re-optimized the structure with fixed Rh–Cp and C_2H_4 units. The result is shown in Fig. 2(B). This M ··· (η^2-H_2C)

Chart 1.

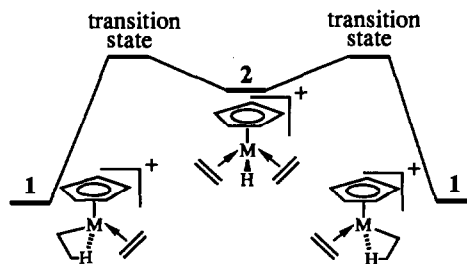species is 6.5 kcal mol⁻¹ higher in energy than the β-agostic complex. The Rh ··· H distances are 2.27 Å and the C–H bonds become 1.11 Å (0.03 Å longer than a normal C–H bond, 1.08 Å).

To examine the other possible process, loss of the (β-agostic interaction and rotation of the methyl group in a 16-electron intermediate, we optimized the non-agostic species by fixing the C–C–Rh bond angle at the tetrahedral angle (109.47°). Figure 2(C) shows the geometry of this species, which is 14.1 kcal mol⁻¹ higher in energy than the β-agostic one. Apparently, the total loss of the agostic interaction before the rotation of the methyl group is very unlikely since it requires such a high activation energy. Therefore, the rotation of the
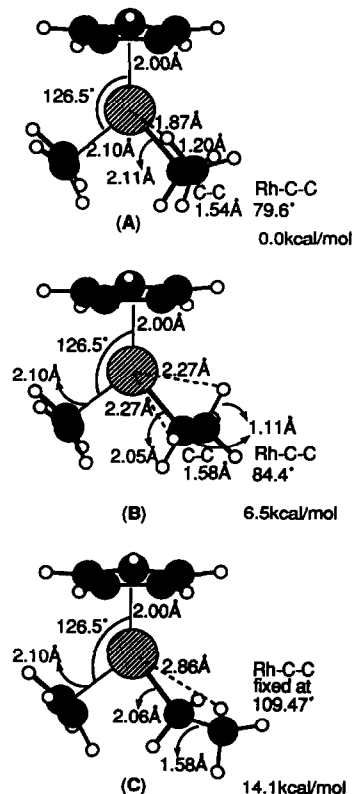

Fig. 2. Optimized structures of the β-agostic complex, [CpRh-$(C_2H_4)(\eta^2$-$C_2H_4)]^+$, (A); a species with Rh ··· (η^2-H_2C) interaction (B); and the non-agostic complex (C).
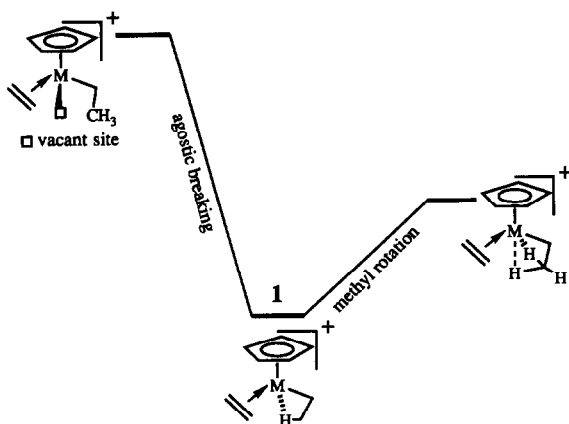
Chart 2.

methyl group in the β-agostic complex occurs through an M $\cdots$ (η^2-H$_2$C) interaction with a calculated activation energy of 6.5 kcal mol^{-1}, a value which is slightly lower than the experimental value of 8.5 kcal mol^{-1}. Chart 2 summarizes the relative energies for different species discussed in this section.

3.3. Exchange of all nine hydrogens and four carbons

This process could occur either through an ethylene rotation or an inversion at the Rh center in a 16-electron intermediate (see Scheme 2). The latter requires the loss of the β-agostic interaction because to invert this structure while retaining the agostic interaction requires a high energy orbital crossing (at least 35 kcal mol^{-1} by our calculations). Thus, the activation energy for the inversion must be at least 14.1 kcal mol^{-1}, the energy difference between the β-agostic (Fig. 2(A)) and non-agostic complex (Fig. 2(C)). If the alternative process, ethylene rotation, requires less activation energy, the inversion process can be excluded. To determine the barrier to the ethylene rotation, we began with the β-agostic structure of Fig. 1(A) and rotated the ethylene by 90.0° about the axis between the Rh and the center of the ethylene. The Rh–ethylene unit was then optimized in this fixed orientation. This optimized geometry, which has a longer Rh–ethylene distance, 2.17 Å, and a shorter C–C bond, 1.43 Å, is 9.8 kcal mol^{-1} higher than the stable β-agostic complex (Fig. 1(A)). In such an ethylene orientation, the complex experiences significant ethylene–Cp repulsive interactions. We predict that this optimized geometry should be very close to the transition state of the ethylene rotation process since the ethylene rotation barrier in most systems was found to be essentially steric in nature [13]. Therefore, the ethylene rotation process has a calculated activation energy of about 9.8 kcal mol^{-1}, a value which is in close agreement with the experimentally reported value (9.6 kcal mol^{-1}). These calculations clearly demonstrate that the inver-
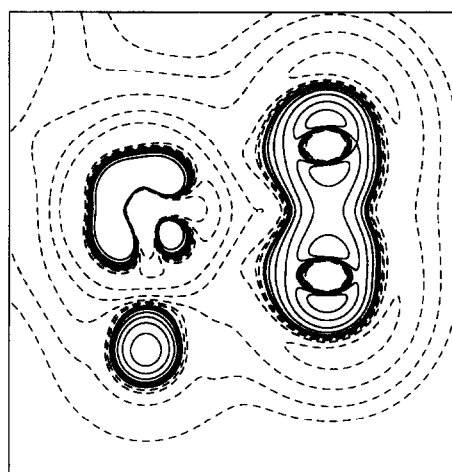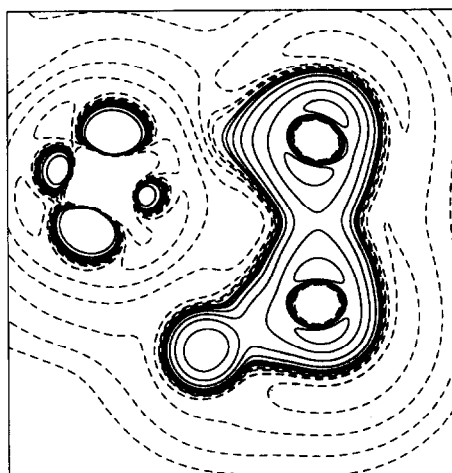
Fig. 3. Plots of $-\nabla^2\rho$ in a plane defined by the H--C--C unit, which is involved in the agostic interaction, for the agostic (top) and its olefin–hydride isomer (bottom) of [CpRh(C$_2$H$_4$)(η^2-C$_2$H$_5$)]$^+$. In the contour display, solid lines denote that the electron density is locally concentrated, and dashed lines denote that the electron density is locally depleted.

sion of the Rh center in a 16-electron intermediate is not responsible for the observed exchange process of all of the nine hydrogens and four carbons.

4. Discussion

4.1. Electron density analysis

To study the nature of agostic interaction, we plot (Fig. 3) the laplacian of the total valence electron density, $-\nabla^2\rho$ [14], for both the β-agostic and olefin–hydride complexes in a plane defined by the H--C--C unit which is involved in the agostic interaction. In the contour plots, solid lines denote $-\nabla^2\rho > 0$, where the electron density is locally concentrated, and dashed lines denote $-\nabla^2\rho < 0$, where the electron density is locally depleted.

The top portion of Fig. 3 shows the laplacian map for the β-agostic complex. It can be seen that when there is significant electron density concentrated between the two atoms, such as the agostic hydrogen and one of the two carbons in the ethyl group, the atoms are considered to be covalently bonded. The agostic hydrogen also interacts with the metal atom through one of the depletions in the metal's valence shell, as is typical for a L → M dative bond. Thus, the metal-agostic interaction can be viewed as a dative C–H → M donation. Since without the agostic interaction the complex has 16 valence electrons, one can describe this agostic interaction as the agostic C–H unit (one pair of electrons) bonded to the central metal atom through its remaining empty orbital. This interaction (a dative C–H → M donation) leads to significant weakening of the C–H bond (0.12 Å longer than a normal C–H bond). Although the electron density around the α-carbon is significantly polarized towards the central metal atom, it is bonded to the metal atom through a depletion in the metal's valence region. Thus, the α-carbon to metal bond could be considered to be between a very polar covalent bond and a strongly donating dative bond.

In the olefin–hydride complex (see the bottom part of Fig. 3), the hydride ligand is bonded to the central metal atom through depletion in the metal's valence region. Figure 3 also shows that more charge is concentrated around the hydride nucleus (bottom) than around the corresponding agostic hydrogen (top). Together these results suggest that the bonding can be formally viewed as H^- bonded to the metal by a strong donor (dative) bond or a very polar covalent bond. The electron density within the ethylene unit is slightly polarized towards the Rh metal center. This polarization results from both metal d electron back-donation to the ethylene unit and the metal–ethylene "σ" bonding.

4.2. Relative stabilities of the β-agostic and olefin-hydride isomers

The electron density analyses above suggest that the charge of Rh is formally $+3$ in both the β-agostic and olefin–hydride complexes. Qualitatively, one can write:

$$E_{agostic} = E_0 + BE(M–C) + BE(M \cdots H–C)$$
$$+ BE(C–H_{agostic}) \quad (1)$$

and

$$E_{olefin-hydride} = E_0 + BE(M–H) + BE(M \leftarrow \|)$$
$$+ BE(C=C's \ \pi) \quad (2)$$

where E_0 represents the total energy for the common bonding units in the β-agostic complex and its olefin–hydride isomer. BE denotes bond energy; for example, $BE(M \leftarrow \|)$ and $BE(M \cdots H–C)$ stand for the bond

energies of the dative metal–ethylene and dative agostic interactions, respectively. Therefore, the energy difference between the two isomers can be approximately formulated as

$$\Delta E \approx \Delta E_1 + \Delta E_2 + \Delta E_3 \quad (3)$$

where

$$\Delta E_1 = BE(M–C) - BE(M–H) \quad (4)$$

$$\Delta E_2 = BE(M \cdots H–C) - BE(M \leftarrow \|) \quad (5)$$

and

$$\Delta E_3 = BE(C–H_{agostic}) - BE(C=C's \ \pi) \quad (6)$$

where ΔE_1 is the bonding energy difference between metal–carbon and metal–hydride. ΔE_2 represents the difference in bond energies between the dative metal–ethylene and dative agostic interactions. ΔE_3 is the difference in bond energies between C–H$_{agostic}$ and C=C's π bonds. These ΔE values are expected to be small because the two bond energies in each ΔE_i ($i = 1$, 2 or 3) are comparable in magnitude. As a result, ΔE is also expected to be small. Examples which support this argument will be cited below.

The strengths of both metal–carbon and metal–hydride bonds increase with increasing size of metal d orbitals. A similar trend applies to the metal–agostic and metal–ethylene interactions. The bond energies of C–H$_{agostic}$ and C=C π bonds depend greatly on the strength of their interaction with the metal atom. The increasing size of metal d orbitals strengthens both the metal–agostic and metal–ethylene interactions, and therefore weakens both the C–H$_{agostic}$ and ethylene π interactions. From the energy difference expressions and the properties of ΔE_1, ΔE_2 and ΔE_3, we do not expect a strong periodic dependence in the energy difference between β-agostic and olefin–hydride complexes since ΔE_1, ΔE_2 and ΔE_3 remain approximately unchanged when the metal atom changes. Such dependence has, however, been found in the relative stabilities of classical and non-classical hydrides [15]. This is because there is a significant change in the metal oxidation state in the conversion from classical to non-classical isomer while the oxidation state of the transition metal remains unchanged when a β-agostic complex is converted to its olefin–hydride isomer.

The implication of the discussion of the energy difference above is that the relative stabilities of a β-agostic complex and its olefin–hydride isomer remain approximately unchanged when the transition metal is replaced by another group member in the Periodic Table. For example, the energy difference between the β-agostic complex and its olefin–hydride isomer for the Co complexes mentioned in the introduction is predicted to be close to that for the corresponding Rh complex. For a complex with different groups of transition metal atoms, the energy difference

is expected to be similar to the system studied here although it will depend on the type and number of ligands in the system. This expectation is confirmed by experimental results where quite a few β-agostic complexes are in rapid equilibrium with their olefin–hydride isomers [1(b)]. For examples, similar equilibria have also been found in systems such as $CpM(CO)_2$ $(\eta^2\text{-}C_2H_5)$ (M=Mo and W) [16].

4.3. Activation barriers

Although the thermodynamic discussion above gives insight into the relative stabilities of the β-agostic complex and its olefin–hydride isomer, it does not provide information about the activation energy for the interconversion process. If we take the structure in Fig. 1(B) as an approximate transition state, we can see that the C--$H_{agostic}$ bond is almost broken in the transition state. A similar transition state has been found in the study of the CH_4 oxidation-addition reaction [17]. Therefore, the relevant activation energy depends substantially on how much the C–$H_{agostic}$ bond is weakened in the ground state of the β-agostic complex. Since a stronger M$\cdots$H–C interaction produces a weaker C–H bond, a transition metal complex with more diffuse metal d orbitals will have a stronger agostic interaction, and therefore, a lower activation energy. This argument is supported by the experimentally observed interconversion process shown in Scheme 1 for Rh and Co complexes. The activation energy for the Rh complex is reported to be 3.7 kcal mol^{-1} while for the Co complex it is 7.2 kcal mol^{-1} [4].

We have shown above that the rotation of the methyl group in the β-agostic complex occurs through an M$\cdots$(η^2-H_2C) interaction. Therefore, the activation energy for the methyl rotation will also depend on the magnitude of the agostic interaction. Again, strong M$\cdots$H–C interactions lower the methyl rotation barrier. For example, the methyl rotation barrier in $[CpCo(L)(\eta^2\text{-}C_2H_5)]^+$ complexes (L = PMe_3, $P(OMe)_3$, C_2H_4) is measured to be ≈ 11 kcal mol^{-1} while it is 8.5 kcal mol^{-1} in the corresponding Rh complex [4]. If complete dissociation of the agostic interactions were involved in the methyl rotation process, one would expect the opposite behavior.

Since the steric effect is essentially responsible for the ethylene-rotation barrier (see Scheme 2 and previous discussion) in the β-agostic complex, the barrier will depend on the sizes of the transition metal and ligands. Generally, for the first row transition-metal complex, the barrier will be greater than the corresponding second row complex. For example, the ethylene-rotation barriers in the $[CpCoLH(C_2H_4)]^+$ complexes (L = PMe_3 or $P(OMe)_3$) are in the range 10–15 kcal mol^{-1} while the corresponding barrier in $[CpRhP(OMe)_3H(C_2H_4)]^+$ is 10.2 kcal mol^{-1} [4a].

5. Conclusion

In the interconversion process shown in Scheme 1 for the $[CpRh(C_2H_4)(\eta^2\text{-}C_2H_5)]^+$ β-agostic complex, its olefin–hydride isomer is found to be an intermediate rather than a transition state. The activation barrier for this process is calculated to be about 5 kcal mol^{-1}. This barrier is inversely proportional to the strength of the agostic interaction since stronger agostic interactions weaken the C–$H_{agostic}$ bond. A higher energy process involving a rotation of the methyl group in the β-agostic complex occurs through an M$\cdots$(η^2-H_2C) interaction with an activation energy of ≈ 6.5 kcal mol^{-1}. Here, a strong M$\cdots$(η^1-HC) interaction will also increase the M$\cdots$(η^2-H_2C) interaction, and therefore, a lower barrier to methyl rotation is predicted. Thus, the barrier for both of these processes varies inversely with the strength of the agostic interaction. Periodically, we expect stronger agostic interactions for those metals with larger (more diffuse) d orbitals. Ethylene rotation in the β-agostic complex is responsible for the final observed process, which exchanges all nine hydrogens and four carbons. The ethylene rotation process depends on the sizes of the transition metal atom and ligands in the complex since steric effects play an important role in the rotation.

Acknowledgments

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