β-Hydrogen Elimination of Five-Membered-Ring Metallacycles. Is It Possible?

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B3LYP density functional theory calculations have been carried out to examine the structural and energetic aspects of β-hydrogen elimination in several metallacyclic complexes of ruthenium and platinum. Factors affecting barriers of the elimination reactions have been examined. It was found that favorable structural arrangements, in which the transferring β-hydrogen is in close proximity to the metal center, for β-hydrogen elimination exist in certain ring conformations of metallacyclic complexes. However, favorable electronic requirements, which allow the transferring β-hydrogen to have effective orbital overlap with the hydride-receiving unoccupied orbital from the metal center, cannot always be achieved. Calculations show that β-hydrogen elimination of several five- and six-membered-ring, 16-electron ruthenium complexes occurs easily. The corresponding reactions of platinum complexes were found to be difficult.

Introduction

β-Hydrogen elimination is an important reaction for a variety of transition-metal complexes containing β-hydrogens, such as metal alkyl complexes,[1−5] metal alkoxide complexes,[6] and so on. In principle, the agostic interaction between a β-hydrogen and the metal center in a given complex can facilitate the corresponding elimination process. It has been suggested that many metallacycles, such as six-, five-, four-, and three-membered metallacycles, cannot undergo β-hydrogen elimination readily, because the M−C_α−C_β−H dihedral angles in these compounds are constrained to values far from 0°.[7] In addition, the β-hydrogen atoms are constrained to positions far away from the metal center. Therefore, the elimination was believed to be difficult. However, there is increasing evidence that β-hydrogen-elimination reactions of five-membered-ring intermediates are possible.[8−10] Questions can be immediately raised. Can metallacycles undergo β-hydrogen elimination, giving hydridometal alkene complexes? If yes, what are the driving forces? Are they related to oxidation states? What is the detailed mechanism? To our knowl-

edge, no systematic theoretical calculations have been carried out to study the β-hydrogen elimination reactions of five-membered-ring metallacyclic complexes. Transition-metal metallacycles are very important intermediates in a wide range of metal-catalyzed reactions,[11] particularly [2 + 2] cycloadditions of olefins,[12] olefin trimerization,[8−9,13−14] [2 + 2 + 2] cycloadditions of diynes,[10,15−19] and alkyne dimerization or trimerization.[20−23] Therefore, we feel it is necessary to theoretically study the β-hydrogen elimination reactions in more detail, in order to understand the intermediates and the transition states. Through our studies, we hope to systematically study the factors influencing the β-hydrogen elimination mechanism. A fundamental understanding of these factors will assist the experimental efforts in finding better catalysts. The ability of ruthenium to assume a wide range of oxidation states and coordination geometries provides opportunities for ca-

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talysis.[24] Therefore, we have chosen several ruthenium complexes as the objects of our study. In this paper, theoretical calculations based on the B3LYP density functional theory have been carried out to examine the structural and energetic aspects of β-hydrogen elimination in several metallacyclic complexes of ruthenium. Square-planar platinum complexes have also been calculated to study the effect of different ligand arrangements.

Computational Details

Molecular geometries of the model complexes were optimized at the Becke3LYP (B3LYP) level of density functional theory.[25] Frequency calculations at the same level of theory have also been performed to identify all the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). On the basis of the frequency calculations, Gibbs free energies were evaluated at 298 K. The Stuttgart/Dresden effective core potentials and basis sets[26] were used to describe Ru, Pt, P, and Cl, while the standard 6-31G basis set was used for C and H atoms. Polarization functions[27] were added for hydrogen ($\zeta(p) = 1.1$), carbon ($\zeta(d) = 0.6$), phosphorus ($\zeta(d) = 0.34$) and chlorine ($\zeta(d) = 0.514$). All the calculations were performed with the Gaussian 98 software package.[28]

To examine the dependability of the B3LYP level of theory, we also employed the BP86 level of theory to optimize the structures related to the $\overline{CpRuCl(CH_2CH_2CH_2CH_2)}$ (**1A**) system. The BP86-optimized structures are almost identical with those optimized at the B3LYP level of theory. The relative energies calculated at the BP86 level for **1A1**, **1A2**, **1TS**, and **1B** are 0.0, 5.5, 9.0, and −0.6 kcal/mol, respectively, in comparison to 0.0, 5.2, 13.5, and 3.4 kcal/mol at the B3LYP level. We further performed single-point CCSD(T) calculations based on the B3LYP-optimzed structures to test the effect of electron correlation. The CCSD(T) relative energies for **1A1**, **1A2**, **1TS**, and **1B** are 0.0, 3.6, 10.2, and −3.7 kcal/mol, respectively. These calculations suggest that the conclusions made in this paper are valid, considering the error introduced by the use of the B3LYP theoretical method.

Results and Discussion

As mentioned in the Introduction, we will focus on the β-hydrogen elimination processes metallacycles → hydridometal alkene complexes (Scheme 1) in this paper. To make sure that hydridometal alkene com-

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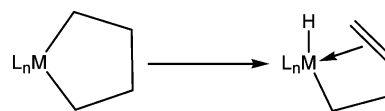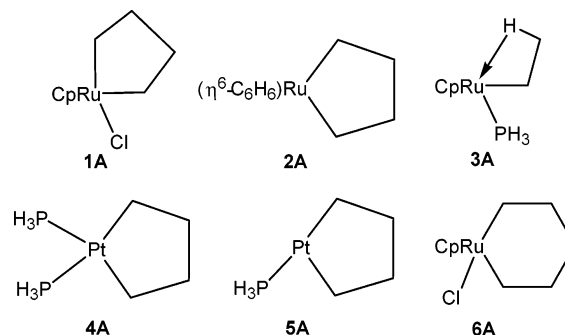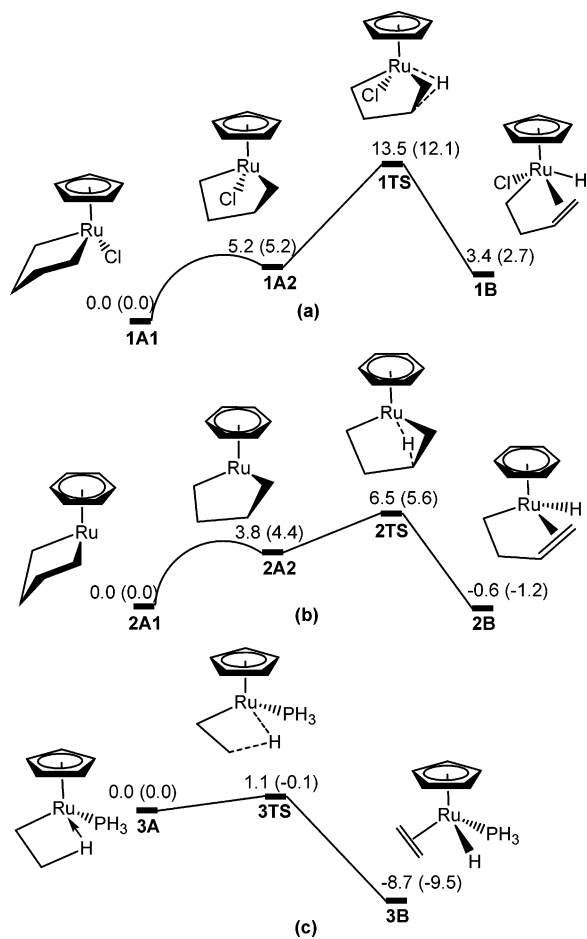
Scheme 1

Chart 1

plexes conform to the 16- or 18-electron rule, we have chosen the 14- or 16-electron species **1A**−**6A** (Chart 1) as the model complexes for metallacycles.

Model complexes **1A** and **2A** are two ruthenium complexes having Ru(IV) and Ru(II) metal centers, respectively. They were chosen for the purpose of examining the effect of oxidation states of the metal centers. Model complex **3A** was also calculated for the purposes of comparison. Model complexes **4A** and **5A** are two platinum complexes with 16- and 14-electron configurations, respectively. Calculations of these two platinum complexes were intended to examine the effect of different ligand arrangements. Model complex **6A** represents an example of six-membered-ring complexes. The calculation results for this complex were used to further exemplify the concepts we intend to develop in this paper.

The potential energy profiles corresponding to the β-hydrogen elimination processes of the first three Ru model complexes (**1A**−**3A**) are shown in Figure 1. As expected, the Ru complex **3A**, which has an agostic bond, undergoes the β-hydrogen elimination reaction with no barrier (1.1 kcal/mol). The agostic interaction facilitates the reaction. Contrary to the common belief that five-membered-ring metallacycles cannot undergo β-hydrogen elimination readily, the elimination reaction of complex **1A** requires only a moderate reaction barrier (8.3 kcal/mol). For the Ru(II) complex **2A**, the reaction barrier (2.7 kcal/mol) is even smaller. In Figure 1 and the following figures, transition states connecting different ring conformational isomers were not calculated. Attempts to locate the corresponding transition states were not successful. We believe that the difficulty in locating the transition states is closely related to the very fluxional feature of the five-membered-ring structures in the complexes studied here. We partially optimized several intermediate structures connecting the ring conformational isomers and found that these intermediate structures lie ca. 7.0 kcal/mol higher in energy than their corresponding lowest energy structures. These additional calculations suggest that the transformation among different conformational isomers also occurs easily. Failure in locating the transformation barriers should not have significant impact on the

Figure 1. Energy profiles for the β-hydrogen elimination reactions of (a) **1A**, (b) **2A**, and (c) **3A**. The relative energies and free energies (in parentheses) are given in kcal/mol.

Figure 2. Selected structural parameters (Å) calculated for species involved in the β-hydrogen elimination reaction of **1A**. The relative energies and free energies (in parentheses) are given in kcal/mol.

Figure 3. Selected structural parameters (Å) calculated for species involved in the β-hydrogen elimination reaction of **2A**. The relative energies and free energies (in parentheses) are given in kcal/mol.

concepts and conclusions we made in this paper regarding the β-hydrogen elimination processes of metallacycles.

The difference in the reaction barriers between the reactions of the two Ru complexes (**1A** and **2A**) is probably due to the following reason. Both complexes **1A** and **2A** are 16-electron species. The presence of the lone-pair electrons on the chloride ligand stabilizes the 16-electron chloride complex **1A**. The structural parameters calculated for **1A**, **1TS**, and **1B** (Figure 2) show that the Ru−Cl bond in **1A** is significantly shorter (2.342 Å) than those in **1TS** (2.454 Å) and **1B** (2.456 Å). The average Ru−C(Cp) distances (ca. 2.27−2.28 Å) in the four structures are close to each other. For the reaction related to the Ru(II) complex (**2A**), there is no such stabilizing effect. **2A1** and **2A2** are relatively less stable, and therefore, the barrier is smaller. The structural parameters of the metal−olefin bonds in **1B** do not differ much from those in **2B** (Figures 2 and 3). Similarly, the two transition structures (**1TS** and **2TS**) resemble each other in the metallacyclic rings (Figures 2 and 3). All these results suggest that the metal−olefin and metal-transferring hydrogen interactions are not responsible for the difference in the two reactions.

The most important question now is why only moderate and small barriers of β-hydrogen elimination were found for the two ruthenium metallacyclic complexes. As shown in Figure 1, complex **1A** (or **2A**) has two conformational isomers. These two conformational iso-
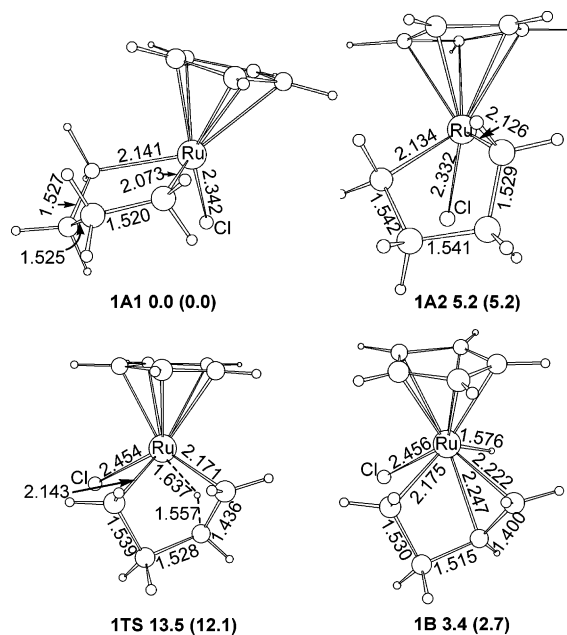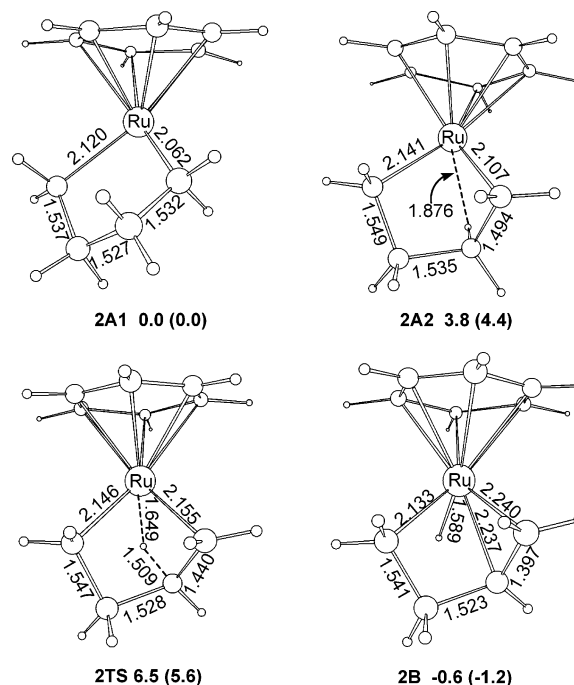
mers are related to the conformational feature of cyclopentane. It is well-known[29−34] that cyclopentane (Chart

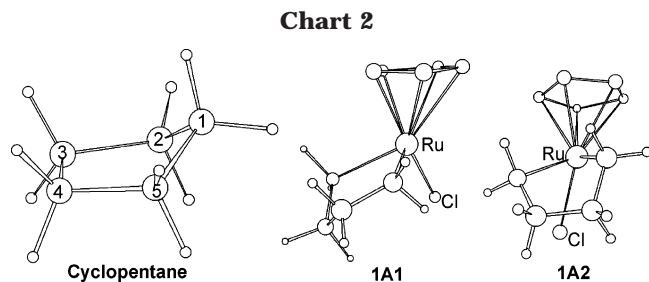(29) Kilpatrick, J. E.; Pitzer, K. S.; Spitzer, R. *J. Am. Chem. Soc.* **1947**, *69*, 2483.
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Chart 2

Figure 4. Energy profiles for the β-hydrogen elimination reactions of (a) **4A** and (b) **5A**. The relative energies and free energies (in parentheses) are given in kcal/mol.

2) actually assumes a slightly puckered "envelope" conformation that reduces the eclipsing and lowers the torsional strain. This puckered shape is not fixed but undulates by the thermal up-and-down motion of the five methylene groups. The "flap" of the envelope seems to move around the ring as the molecule undulates.[35] Our calculations suggest that the five-membered rings in the two isomers also have an envelope conformation. Chart 2 shows the structures calculated for these two isomers. The hydrogen atoms of the Cp ring have been omitted for the purpose of clarity.

In principle, there are six possible conformational isomers for a metallacyclopentane Cp complex, in consideration of the three types of unique positions in the five-membered ring (see the cyclopentane structure of Chart 2) and different orientations of the Cp ligand. We only located two minimum structures (**1A1** and **1A2**). Attempts to locate other conformational isomers failed. This could suggest that there exist only two local minima on the potential surface at this level of theory. **1A2** is higher in energy than **1A1** by 5.2 kcal/mol. The instability of **1A2** can be conveniently related to the fact that there are greater repulsive interactions between the "flap" CH$_2$ group and the Cp ligand.

As shown in Figure 1a, **1TS** corresponds to the transition state for the β-hydrogen elimination process. The intrinsic reaction coordinate (IRC) calculations show that the transition structure (**1TS**) connects the isomer **1A2** of the metallacyclic complex **1A** and the β-hydrogen-eliminated product **1B**. Isomers **1A1** and **1A2** are both 16-electron species. They can be described as being derived from a four-legged piano-stool structure in which one leg is missing. Because of their 16-electron configurations, isomers **1A1** and **1A2** are both coordinatively unsaturated. Each isomer is expected to have a low-lying unoccupied orbital, which is ready to accept the β-hydrogen to form the metal–hydride bond in the eliminated product. It is also expected that the low-lying unoccupied orbital should have the maximum amplitude along the direction of the missing site (leg) in the parent four-legged piano-stool structure. Chart 3 illustrates schematically the low-lying orbital for each of the two conformational isomers of complex **1A**. It can be seen from Chart 3 that in **1A1** all the β-hydrogens orient themselves away from the maximum amplitude of the low-lying unoccupied orbital. However, there is a β-hydrogen (marked with an asterisk in Chart 3) in close proximity to the maximum amplitude of the low-lying unoccupied orbital in the direction of the missing site. The reason the transition structure connects **1A2**, rather than **1A1**, and **1B** is now understood. In **1A2**, the close proximity of the transferring β-hydrogen to the
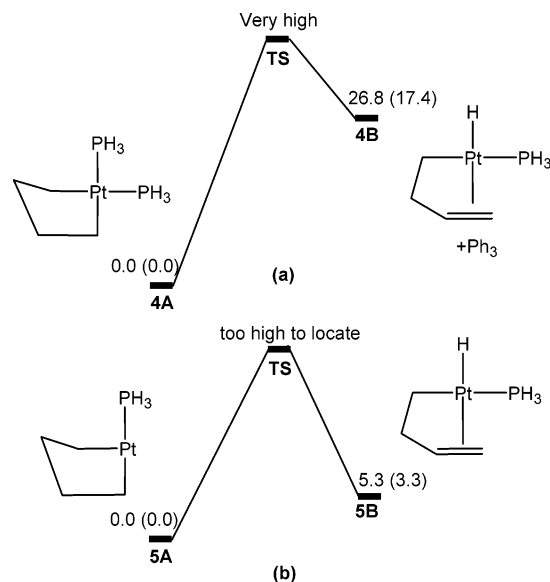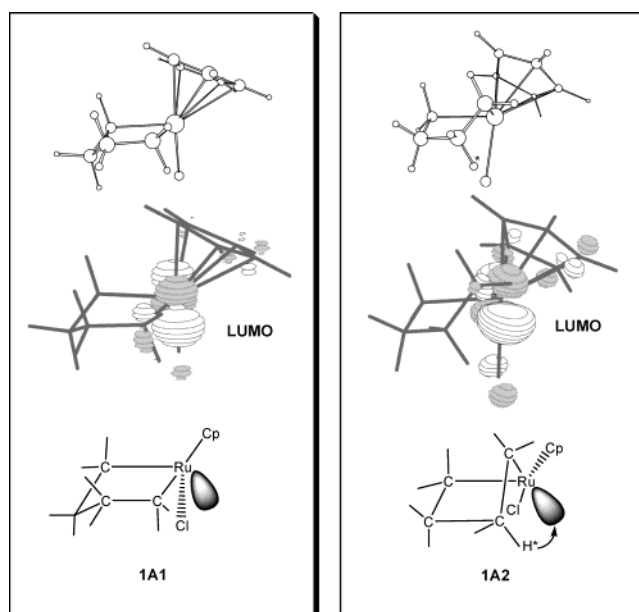
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Chart 3

accepting unoccupied orbital is essential to facilitate the β-hydrogen elimination process.

The arguments above can also be used to understand the results calculated for complex **2A**. The structural features of **2A1** and **2A2** resemble those of **1A1** and **1A2**, respectively. Again, we see that **2TS** connects the isomer **2A2**, rather than **2A1,** and the eliminated product **2B**. **2B** assumes a three-legged piano-stool structure, showing the metal–olefin bonding interaction (Figure 3).

Complexes of platinum(II) normally adopt a square-planar structure and conform to the 16-electron rule. It is interesting to see if it is possible for metallacyclopentane complexes of platinum(II) to undergo β-hydrogen elimination. Unexpectedly, the reaction barrier of the β-hydrogen elimination from the model complex **4A** was found to be very high (Figure 4a). We failed to locate the transition state. This could be due to the fact that the transition structure is very high in energy and

4A 0.0 (0.0)   **4B 26.8 (17.4)**
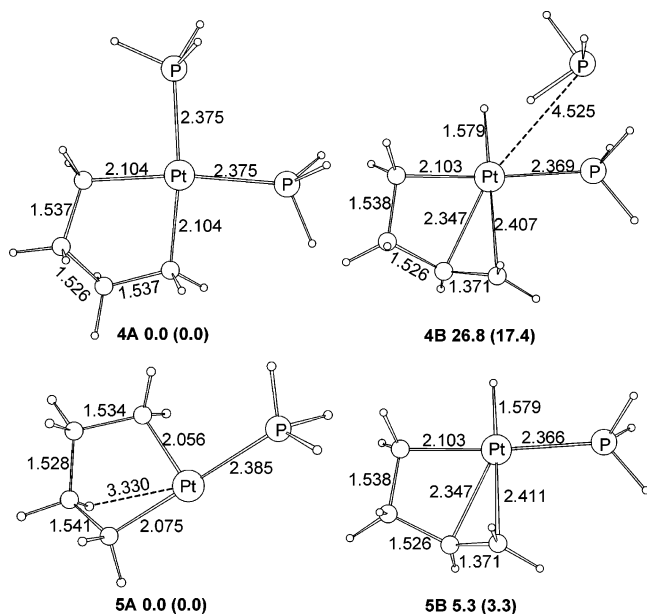
5A 0.0 (0.0)   **5B 5.3 (3.3)**

Figure 5. Selected structural parameters (Å) calculated for species involved in the β-hydrogen elimination reactions of **4A** and **5A**. The relative energies and free energies (in parentheses) are given in kcal/mol.

resides at the maximum energy point along the reaction coordinate of the potential energy surface, which has an enormously large curvature, making it difficult to locate. Even with a 14-electron complex (**5A**), the transition state for the β-hydrogen elimination process is again too high to locate (Figure 4b) for the same reason.

Our calculations show that we can only locate one conformational isomer for complexes **4A** and **5A** (Figure 5). The conformational feature of the structures calculated for **4A** and **5A** resembles that of **1A1** or **2A1**. The β-hydrogens in the structure are not in the optimal positions for β-hydrogen elimination, as pointed out above. Despite the unfavorable orientations of the β-hydrogens, one can always assume a pseudorotation to obtain a suitable conformational structure having one of the β-hydrogens in close proximity to the metal center.

Scheme 2 illustrates such a pseudorotation process. **4A′** has a conformational feature allowing the β-hydrogen elimination to occur. The very high reaction barrier for the β-hydrogen elimination reaction of **4A** suggests that the empty coordination site at the Pt center of **4A′** is not exactly empty. For a square-planar d^8 species, such as **4A** or **4A′**, the eight d electrons occupy the "t$_{2g}$" and d$_{z^2}$ orbitals. Here, the z axis is defined to be perpendicular to the square plane. Apparently, the electrons residing in the d$_{z^2}$ orbital prevent the hydride migration to the metal center (see Scheme 2). The p$_z$ empty orbital of Pt does not play a role, because of its high orbital energy.

For the 14-electron complex **5A**, the maximum amplitude of the empty orbital derived from the real vacant site is still too far away from the β-hydrogen to make the elimination possible (Chart 4).

To further exemplify the findings discussed above, we also studied the β-hydrogen elimination of complex **6A**, an example of a six-membered-ring metallacyclic complex. Molecules having a six-membered ring normally
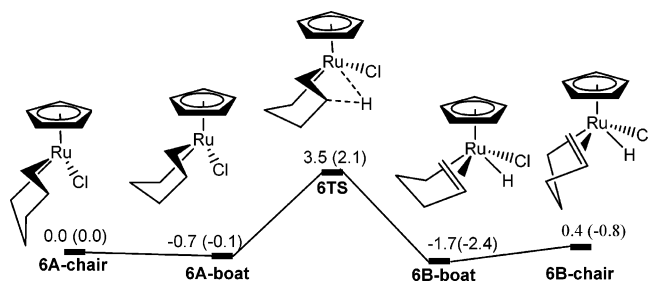

Figure 6. Energy profiles for the β-hydrogen elimination reactions of **6A**. The relative energies and free energies (in parentheses) are given in kcal/mol.
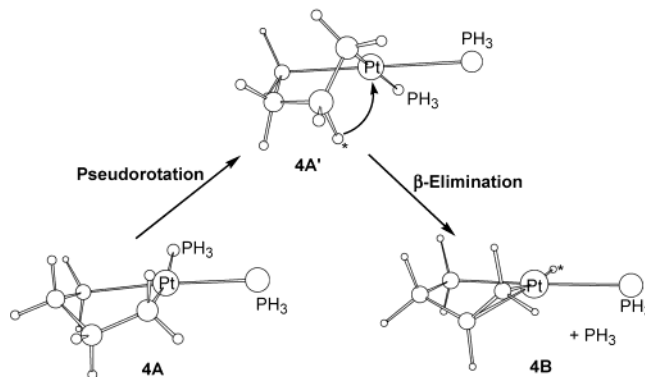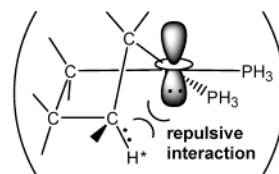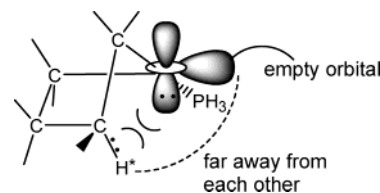
Scheme 2

Chart 4

adopt a chair or boat conformation. Our calculations show that the chair and boat isomers of complex **6A** both correspond to local minima on the potential energy surface. The boat isomer (**6A-boat**) is only slightly lower in energy than the chair isomer (**6A-chair**) (see Figure 6). Comparing the conformational features of **6A-chair** (or **6A-boat**) and the envelop conformer **1A2**, we found that they resemble each other, particularly in the orientations of the transferring hydrogens. It is, therefore, expected that the β-hydrogen elimination of **6A** is possible. Indeed, calculations show that the barrier for the elimination is only about 4.2 kcal/mol (Figure 6). Interestingly, the transition state **6TS** connects **6A-boat** and **6B-boat**. The transition state has also a boat conformation. Careful examination of the structures of the **6B-boat** and **6B-chair** isomers (Figure 7) allows us to understand the reason the transition state does not connect the two chair structures **6A-chair** and **6B-chair**. In both **6B-boat** and **6B-chair**, the hydrogen atom bonded to the olefinic β-carbon has a cis arrangement with respect to the hydride ligand. This structural feature suggests that the whole CH$_2$ unit, whose carbon
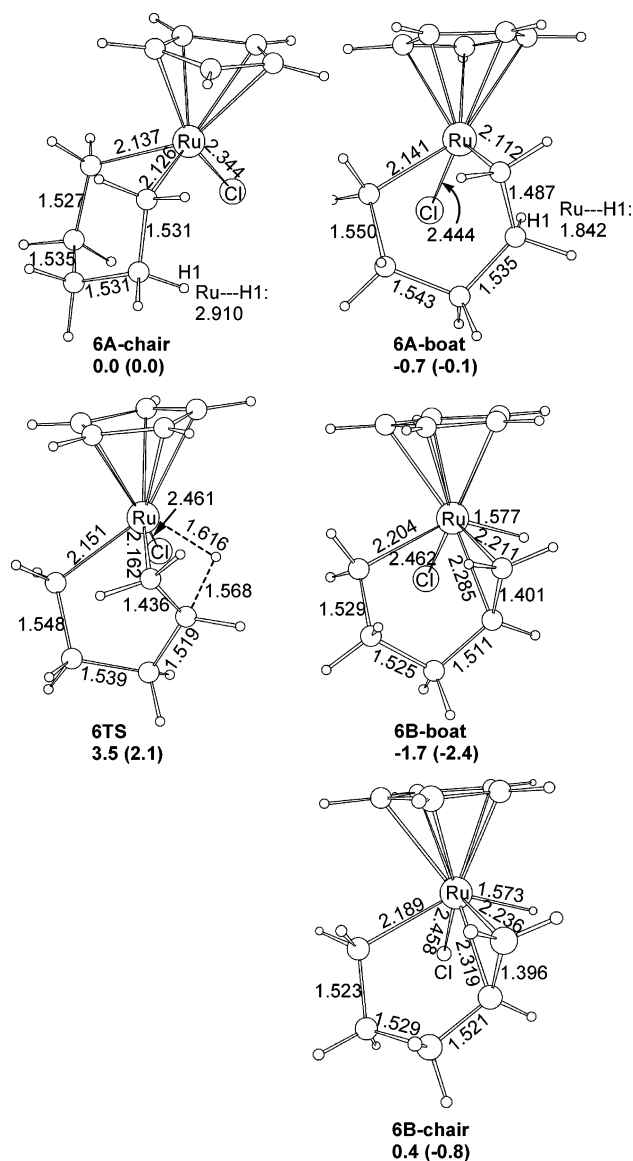
Figure 7. Selected structural parameters (Å) calculated for species involved in the β-hydrogen elimination reaction of **6A**. The relative energies and free energies (in parentheses) are given in kcal/mol.

becomes the olefinic β-carbon in the β-hydrogen-eliminated product (**6B-boat** or **6B-chair**), rotates along the C_β–C_γ bond during the hydrogen-transferring process. It is the CH_2 rotation that makes the transition state assume a more boatlike structure. **6B-chair** is calculated to be slightly less stable than **6B-boat**. Indeed, several relevant complexes are known to adopt structures similar to **6B-boat**, although structures having the **6B-chair**-like conformation can also be found.[36]

Conclusions

In this paper, β-hydrogen elimination of several ruthenium and platinum metallacycles has been theo-

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retically investigated. Our calculations indicate that the β-hydrogen elimination reactions of five- or six-membered-ring, 16-electron ruthenium metallacycles are thermodynamically and kinetically feasible. In contrast, the β-hydrogen elimination reactions of platinum metallacycles were found to be very unfavorable.

Structural and bonding analyses show that five-membered-ring ruthenium complexes can adopt a ring conformation in which the transferring β-hydrogen not only is in close proximity to the metal center but also orients itself in such a direction that allows effective orbital overlap with the low-lying unoccupied orbital commonly found for a 16-electron nonplanar metal complex and facilitates the β-hydrogen elimination reaction. The maximum amplitude of the low-lying orbital of a 16-electron complex is normally found in the direction of the missing coordination site derived from its parent 18-electron complex. Sixteen-electron, six-membered-ring ruthenium complexes adopt either chair or boat conformations which also have the structural and electronic features that favor the β-hydrogen elimination reactions.

The square-planar 16-electron complexes studied here can also assume ring conformations similar to those found for the ruthenium complexes and having the transferring β-hydrogen in close proximity to the metal center. However, the maximum amplitudes of the low-lying unoccupied p_z orbital coincide in directions with those of the occupied d_{z^2} orbital. Here, the z axis is defined as being perpendicular to the molecular plane of the metal complex. Therefore, the repulsive interaction between the C–H (transferring hydrogen) bond and the electron pair residing in the d_{z^2} orbital predominates and prevents the β-hydrogen transfer from occurring. Even with a 14-electron planar metallacyclic complex, the repulsive interactions still dominate and the maximum amplitude of the low-lying orbital derived from the missing ligand (with respect to the 16-electron parent complex) is far away from the metal center. We hope that experimentalists will in the future test the conclusions made here.

It should be pointed out here that β-hydrogen elimination reactions give hydridometal alkene complexes. The strong metal–alkene bonding interactions contribute significantly to the stability of the β-hydrogen-eliminated product and lower the elimination barriers. Therefore, it is expected that for d^0 metallacyclic complexes the corresponding β-hydrogen elimination reactions have significantly high barriers because of the much weaker metal–alkene interactions due to the lack of metal (d)-to-alkene (π^*) back-bonding interactions.[8,9]

Supporting Information Available: Tables giving Cartesian coordinates of all the calculated structures reported in this article. This material is available free of charge via the Internet at http://pubs.acs.org.