取代基对有机铬化合物分子内氢转移反应势垒的影响

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摘要: 使用密度泛函理论 B3LYP 方法研究了取代基对一系列有机 Cr 化合物 $(R_3)(R_4)Cr(\equiv CH)(CHR_1R_2)$ 分子内 α-H 转移反应能垒的影响。确定了反应物、过渡态和产物的几何结构和反应势垒。研究结果表明,当 R_1 和 R_2 是甲基,R_3 和 R_4 是 PH_2 基团、Silyl 基团或 Cl 原子时,反应势垒最低。

Effect of Substituent on the Reaction Barrier of Intramolecular α-hydrogen Transfer from Alkyl to Alkylidyne Ligand in Organochromium Complexes

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Abstract: Density functional theory B3LYP method is carried out to investigate the effect of substituent on the reaction barrier of intramolecular α-hydrogen transfer from alkyl to alkylidyne ligands in a series of organometallic chromium complexes $(R_3)(R_4)Cr(\equiv CH)(CHR_1R_2)$. The optimal structures of reactants, transition states and products are obtained. The reaction barriers are then estimated. Calculation results indicate that the most preferable substituent is a methyl group for R_1 and/or R_2. For R_3 and/or R_4, the favorite substituent is a PH_2 group or a silyl group or a chlorine atom.

Key words: organometallic chromium complex; intramolecular hydrogen transfer; reaction barrier

0   Introduction

　　High oxidation state transition metal alkylidyne (L_nMCR) and alkylidene ($L_nM=CR_2$) complexes have been of great interest, not only because of their unique structure and bonding properties but also because of their relevance to organic synthesis and catalysis [1,2]. The first "high oxidation state" transition metal complexes that contain a multiple metal-carbon bond were discovered about 30 years ago in the form of (η^5-$C_5H_5)_2Ta$ (=CH_2) (CH_3) [3] and ($Bu^tCH_2)_3Ta$ (=$CHBu^t$) [4].

Since that time, interest in high oxidation state alkylidene (M=CR_1R_2) and alkylidyne (MCR) complexes has grown considerably. It could be argued that interest in the catalytic metathesis of alkenes and alkynes was the driving force for the development of "high oxidation state" (d^0) alkylidene and alkylidyne chemistry. The α-hydrogen atoms play a pivotal role in the synthesis of high oxidation state transition metal alkylidene and alkylidyne complexes[5]. Alkylidyne complexes are often formed from alkylidene complexes by α hydrogen abstraction reactions (or vice versa). The α-hydrogen

atoms in a number of alkylidyne and alkylidene complexes have been found to undergo exchanges among the α-carbon atoms. Indeed, α-hydrogen abstraction is believed to be one of the primary reactions leading to metal-carbon multiple bonds, as was seen in Schrock′s initial synthesis of $(Bu^tCH_2)_3Ta$ $(=CHBu^t)^{[4]}$. It is believed that $Ta(CH_2Bu^t)_5$ rapidly decomposes to $(Bu^tCH_2)_3Ta(=CHBu^t)$ after a relatively slow reaction between $Ta(CH_2Bu^t)_3Cl_2$ and an alkylating agent (even $LiCH_2Bu^t$) that leads to its formation. The thermochemistry of the decomposition of $Ta(CH_2SiMe_3)_5$ to give $(Me_3SiCH_2)_3Ta(=CHSiMe_3)$ by a hydrogen abstraction has been quantified[6].

The α-hydrogen atom in d^0 alkyl alkylidyne complexes $(RCH_2)_3WCR$ are also known to undergo exchanges among the α-carbon atoms, leading to alkyl-alkylidyne scrambling in $(Bu^tCH_2)_3WCBu^t$ and $(Bu^tCH_2)_3$ $WCSiMe_3^{[7]}$. Deuterium-labeling and kinetic studies of the α-hydrogen migration in $(Bu^tCH_2)_3WCSiMe_3$ showed stepwise transfer of two hydrogen atoms in one alkyl ligand to the alkylidyne ligand with a proposed bis(alkylidene) intermediate $(Bu^tCH_2)_2W(=CHSiMe_3)(CHBu^t)^{[7b]}$. The α-hydrogen atoms in a d^2 bis (alkylidene) complex $Os(=CHBu^t)_2(CD_2Bu^t)_2$, hydrogen/deuterium atoms were also found to scramble among the α-carbon atoms at 0 ℃[8].

A phosphine-promoted exchange $(Me_3SiCH_2)_3W$ $(CSiMe_3)(PMe_3)$ and $(Me_3SiCH_2)_2W(CSiMe_3)_2(PMe_3)$ was also reported [9]. In the absence of phosphine, bis (alkylidene) "$(Me_3SiCH_2)_2$" was not observed. d^0 Silyl alkylidyne complex $(Bu^tCH_2)_2W(CBu^t)(SiBu^tPH_2)$ was found to exchange with its bis (alkylidene) tautomer $(Bu^tCH_2)W(=CHBu^t)_2(SiBu^tPH_2)^{[10]}$. The silyl ligand plays an important role in this alkyl alkylidyne-bis (alkylidene) exchange, as no such exchange has been directly observed in $(Bu^tCH_2)_3W^{13}CBu^t$ and the alkyl analog[7a].

The relative stability of the reactant and the product of α-hydrogen shift reaction in several transision organometallic complexes were theoretically studied by Choi and co-workers[11]. We investigated the transition structures and reaction barriers of the intramolecular α-hydrogen transfer reaction in some organometallic tungsten complexes and molybdenum

complexes[12]. In this paper, α-hydrogen shift reactions of the organometallic chromium complexes were investigated and the reaction barriers were evaluated, the effects of the different substituents on the reaction barriers of the intramolecular α-hydrogen shift reactions were then discussed.

1　Computational details

As shown in Scheme 1, the model complexes **A** and **B** are used to mimic the tautomeric structures of transition metal alkylidyne and bis (alkylidene) complexes, respectively. The model complex **C** is used to simulate the transition state structure between the tautomers. In order to examine the effect of the substituent on the reaction barrier of intramolecular α-hydrogen transfer reaction, fourteen reactions (Scheme 1) are designed and studied with the B3LYP method[13~15] in the Gaussian 03 program[16].
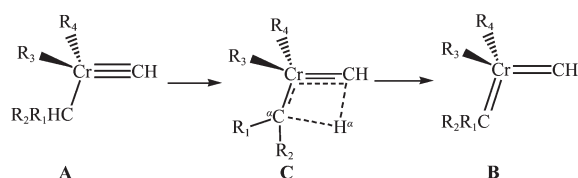
1	R_1=H, R_2=Me, R_3=Me, R_4=Me
2	R_1=H, R_2=SiH$_3$, R_3=Me, R_4=Me
3	R_1=H, R_2=F, R_3=Me, R_4=Me
4	R_1=H, R_2=H, R_3=Me, R_4=Me
5	R_1=Me, R_2=Me, R_3=Me, R_4=Me
6	R_1=F, R_2=F, R_3=Me, R_4=Me
7	R_1=H, R_2=H, R_3=Me, R_4=CF$_3$
8	R_1=H, R_2=H, R_3=Me, R_4=F
9	R_1=H, R_2=H, R_3=Me, R_4=Cl
10	R_1=H, R_2=H, R_3=Me, R_4=PH$_2$
11	R_1=H, R_2=H, R_3=PH$_2$, R_4=PH$_2$
12	R_1=Me, R_2=Me, R_3=PH$_2$, R_4=PH$_2$
13	R_1=Me, R_2=Me, R_3=SiH$_3$, R_4=SiH$_3$
14	R_1=Me, R_2=Me, R_3=Cl, R_4=Cl

α-carbon atom and α-hydrogen atom are shown in the transition state

Scheme 1　Fourteen intramolecular α-hydrogen shift reactions studied in this paper

Geometric optimizations for all model complexes are carried out at the B3LYP level. Transition metal atom is described by the effective core potentials (ECPs) of Wadt and Hay [17] with a double-ξ valence

basis set, and the standard 6-31G (d) basis set are used for hydrogen, carbon, fluorine, silicon, phosphor, and chlorine atoms. Harmonic frequencies are calculated to characterize stationary states as local minima (all real frequencies) and first-order saddle points (one imaginary frequency). Single point energies are further evaluated with B3LYP method. The basis sets in the single-point calculations are SDDAll basis set for chromium atom and 6-311++G (d,p) basis set for the other atoms. The SDDAll effective core potentials are used in the single-point calculations for chromium atom. For the transition metal chromium atom, the f polarization functions[18] are also included in the single-point calculations. The relative energies are corrected with zero-point-energy (ZPE).

2　Results and discussions

2.1　Transition state structures

　　The optimized transition state structures are shown in Fig.1, together with some selected structural parameters. β is the dihedral angle between R_1-C^{α}-Cr plane and Cr-C^{α}-R_2 plane (see model complex **C** in Scheme 1). It can be seen from Fig.1 that all fourteen transition state structures adopt a distorted trigonal-pyramidal geometry, no matter what the ligands are. As shown in Fig.1, the transition states all have quite similar geometry with a C^{α}–Cr≡C angle of about 100° (the differences in bond angle within 5° ~10° for different ligands). The bond lengths between the α-carbon atoms, from which the α-hydrogen atom has
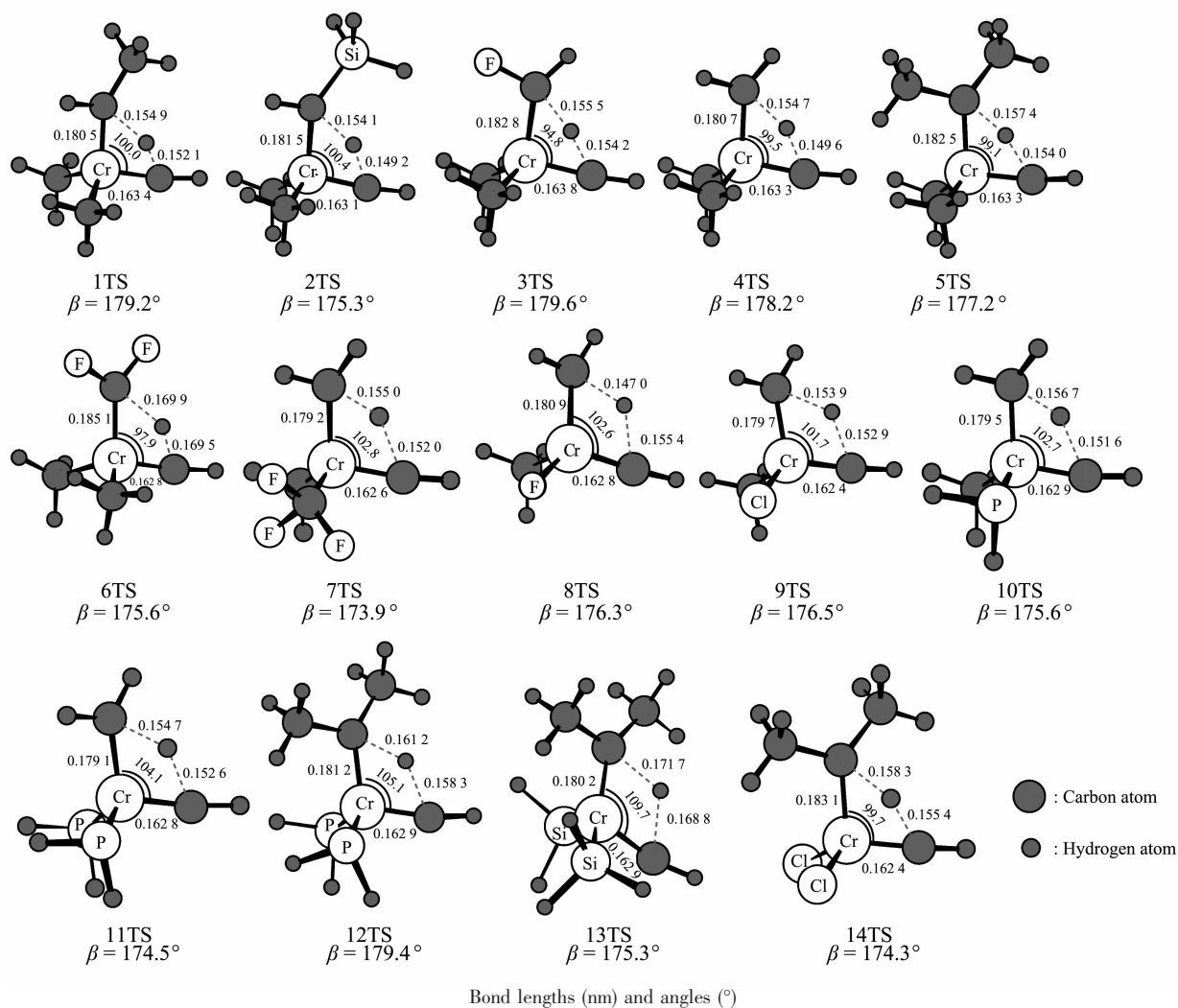

Bond lengths (nm) and angles (°)

Fig.1　Optimal transition state structures for the fourteen reactions studied in this paper, β are the dihedral angles between R_1-C^{α}-Cr plane and Cr-C^{α}-R_2 plane (see model complex **C** in Scheme 1)

shifted, and the metal chromium are 0.180 nm or so. The bond lengths between the carbon atoms, to which the α-hydrogen atom has shifted, and the metal chromium are 0.163 nm or so. The dihedral angle β varies from 173.9° to 179.6°. For instance, the dihedral angle β is 179.2° for the transition state structure of the reaction **1** where R$_1$ is a hydrogen atom and R$_2$ is a methyl group. The dihedral angle β is 178.2° for the transition state structure of the reaction **4** where both R$_1$ and R$_2$ are hydrogen atoms. The dihedral angle β is 177.2° for the transition state structure of the reaction **5** where both R$_1$ and R$_2$ are methyl groups. The smallest dihedral angle β is 173.9° found for the transition state structure 7TS of the reaction **7** where R$_3$ is a methyl group and R$_4$ is a CF$_3$ group. These demonstrate that the α-carbon atom, the metal atom, and the two central atoms of R$_1$ and R$_2$ are nearly on the same plane and

indicate that the α-carbon atom adopts the sp^2 hybridization in the transition state. Therefore, it can be reasonably deduced that the reaction barrier will be lowered if the substituent can delocalize the electron in p_z orbital of the α-carbon atom.

2.2 Effect of substituent R$_1$ or R$_2$ on reaction barrier

Scheme 1 shows that for the reactions **1~4**, the only difference is the R$_2$ group. Table 1 shows that the highest reaction barrier (133.8 kJ·mol^{-1}) exists when R$_2$ group is a hydrogen atom while the reaction has the lowest reaction barrier (114.9 kJ·mol^{-1}) when R$_2$ is a methyl group. When R$_2$ is a fluorine atom or a silyl group, the reaction barriers are 129.0 and 128.8 kJ·mol^{-1}, respectively. They are lower than that of reaction **4** where R$_2$ is a hydrogen atom and higher than that of reaction **1** where R$_2$ is a methyl group.

Table 1 Relative energies (kJ·mol^{-1})

Reaction	R$_1$	R$_2$	R$_3$	R$_4$	Reactant	Transition state	Produnct
1	H	Me	Me	Me	0	114.9	15.68
2	H	SiH$_3$	Me	Me	0	128.8	25.8
3	H	F	Me	Me	0	129	21.9
4	H	H	Me	Me	0	133.8	39.8
5	Me	Me	Me	Me	0	106.9	5.2
6	F	F	Me	Me	0	108.2	−20.6
7	H	H	Me	CF$_3$	0	132.1	18.1
8	H	H	Me	F	0	132.1	25.2
9	H	H	Me	Cl	0	125	41.6
10	H	H	Me	PH$_2$	0	125.6	27.7
11	H	H	PH$_2$	PH$_2$	0	122.5	46.8
12	Me	Me	PH$_2$	PH$_2$	0	89.7	15.8
13	Me	Me	SiH$_3$	SiH$_3$	0	89.4	26.4
14	Me	Me	Cl	Cl	0	87.8	−0.84

The changes in the reaction barriers of the reactions **1~4** can be well understood from the orbital interaction. Fig.2 and Fig.3 show the orbital interactions in these systems. As depicted in Fig.2(a), when R$_2$ is a hydrogen atom, the overlap between the s orbital of the hydrogen atom and the p_z orbital of the α-carbon atom is zero, which leads to no effective bonding between these two orbitals, indicating that a hydrogen atom in R$_1$ or R$_2$ position cannot stabilize the electron in α-carbon p_z orbital. Therefore, the reaction barrier is high when R$_2$ is a hydrogen atom (133.8 kJ·mol^{-1}).
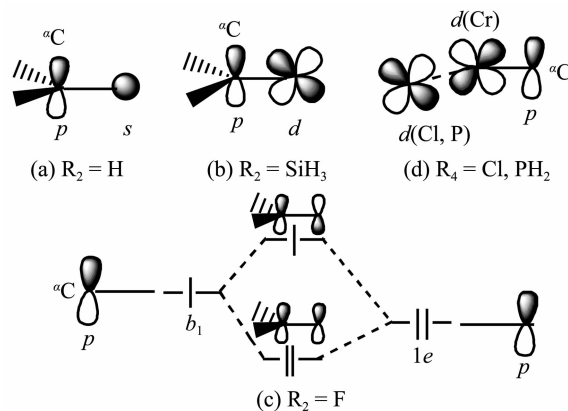

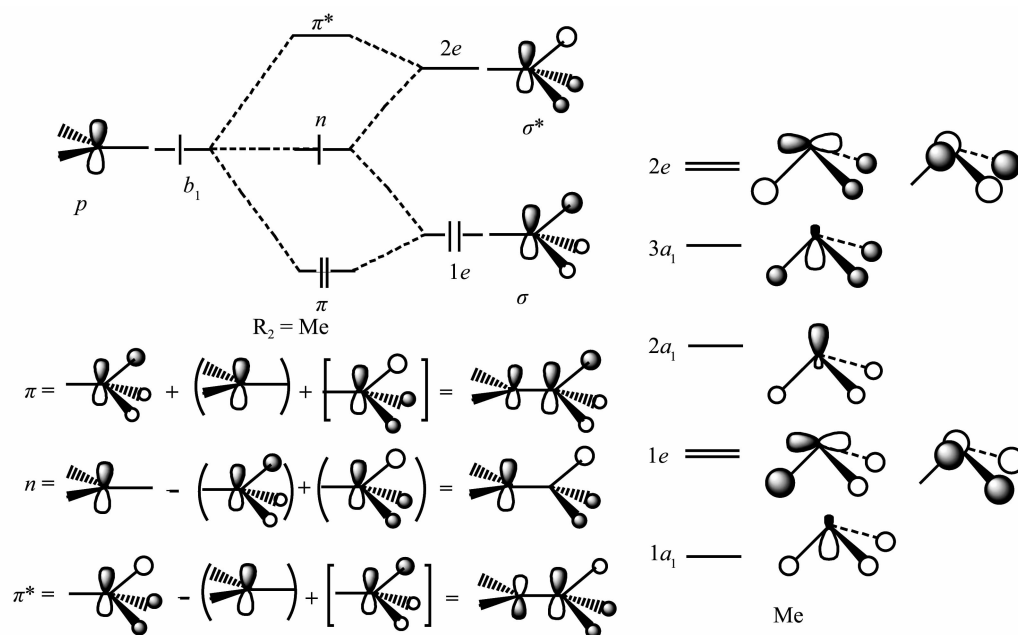Fig.2 Overlap of the atomic orbitals

Fig.3　Overlap of the atomic orbitals in transition states of R$_2$=CH$_3$

Fig.3 shows the overlap between the methyl orbitals and the α-carbon p_z orbital at the left-hand. At the right-hand of Fig.3 are the seven valence orbitals of the methyl group. As shown at the right-hand of Fig.3, $1a_1$ and $1e$ are three double occupied bonding molecular orbitals, $2a_1$ is a single occupied molecular orbital, and $3a_1$ and $2e$ are three unoccupied antibonding molecular orbitals. When R$_2$ is a methyl group (as in the reaction **1**), the single occupied $2a_1$ orbital of the methyl group is used to form a σ-bonding orbital with one of the sp^2 hybridization orbitals of the α-carbon atom. According to the perturbation theory[19], the unhybridized p_z orbital of the α-carbon atom combines with one $1e$ orbital and one $2e$ orbital of the methyl group as shown at the left-hand of Fig.3, which gives rise to one bonding orbital π, one nonbonding orbital n and one antibonding orbital π^*. Two electrons fill in the bonding orbital π and one electron fills in the nonbonding orbital n, two electrons are thus stabilized. Therefore, the reaction barrier (114.9 kJ$\cdot$mol^{-1}) is lowered substantially compared with that when R$_2$ is a hydrogen atom (133.8 kJ$\cdot$mol^{-1}).

Fig.2 (b) shows that the p_z orbital of the α-carbon atom can overlap with one of the d orbitals of the SiH$_3$ group if they are symmetry-adapted. When R$_2$ is a silyl group, a certain bonding interaction exists between the p_z orbital of the α-carbon atom and the d orbital of the silyl group, this stabilizes the unpaired electron in the p_z orbital of α-carbon in some degree. But the effective orbital overlap in Fig.2 (b) is smaller than in Fig.3 because C-Si bond length (0.186 nm) is longer than C-C bond length (0.154 nm) and because of the atomic orbital energy difference between the d orbital of the silicon atom and the p orbital of the carbon atom. Consequently, the reaction barrier (128.8 kJ$\cdot$mol^{-1}) is lowered when R$_2$ is a silyl group compared with when R$_2$ is a hydrogen atom (133.8 kJ$\cdot$mol^{-1}), but not as low as when R$_2$ is a methyl group (114.9 kJ$\cdot$mol^{-1}).

Fig.2(c) shows that the p_z orbital of the α-carbon atom can overlap with the p_z orbital of the fluorine atom, leading to one bonding π molecular orbital and one antibonding π molecular orbital. Two electrons occupy the π bonding molecular orbital, another one fills in the π^* antibonding molecular orbital. Therefore, two electrons are stabilized and one electron is unstabilized. The reaction barrier is thus lowered. The perturbation theory indicates that the rise of the antibonding orbital level is more than the fall of the bonding orbital level[19]. Therefore, for the reaction **3** where R$_2$ is a fluorine atom, the reaction barrier (129.0 kJ$\cdot$mol^{-1}) is lower than that of the reaction **4** where R$_2$ is a hydrogen atom (133.8 kJ$\cdot$mol^{-1}) but higher than that of the reaction **1**

where R_2 is a methyl group （114.9 kJ·mol^{-1}). These results are also in agreement with the results about the effect of the substituents on the dissociation energy of the organic compound C-H bond[20,21].

We can reasonably deduce that if both R_1 and R_2 are methyl groups, the reaction barrier should be even lower than that of the reaction **1**. In order to check this guess, the reaction **5** was designed and the similar calculations were performed on it. The data are also collected in Table 1. Table 1 shows that the reaction barrier of the reaction **5** is only 106.9 kJ·mol^{-1}, 8.0 kJ·mol^{-1} lower than that of the reaction 1, consistent with our deduction. We also designed the reaction **6** where both R_1 and R_2 are fluorine atoms. As what we expected, calculation results show again that the reaction **6**, where both R_1 and R_2 are fluorine atoms, has a lower reaction barrier (108.2 kJ·mol^{-1}) than the reaction **3**, where R_2 is a fluorine atom but R_1 is a hydrogen atom （129.0 kJ·mol^{-1}).

2.3   Effect of substituent R_3 or R_4 on reaction barrier

As shown in Scheme 1, in the reactions **4**, **7**, **8**, **9**, and **10**, only R_4 group is different. The data in Table 1 show that the reaction barrier of the reactions **4**, **7**, **8**, **9**, and **10** are 133.8, 132.1, 132.1, 125.0, 125.6 kJ·mol^{-1}, respectively. Among them, the high reaction barriers (133.8, 132.1, 132.1 kJ·mol^{-1}) are found for the reactions **4**, **7**, and **8** where R_4 are a methyl group, a CF_3 group, and a fluorine atom, respectively. The low reaction barriers （125.0 and 125.6 kJ·mol^{-1}) are found for reactions **9** and **10** where R_4 are a PH$_2$ group and a chlorine atom, respectively.

From the orbital interaction point of view, R_4 group can to a certain extent interact with the p_z orbital of the α-carbon through the 3d orbital of the metal chromium atom if they are symmetry-adapted. It can be seen from Fig.2 （d) that for the reactions **9** and **10**, where R_4 are a chlorine atom and PH$_2$ group, respectively, one of the 3d orbital of the chlorine or phosphor atom and one of the 3d orbital of the metal atom can overlap with each other. The 3d orbital of the metal and the 2p_z orbital of the α-carbon atom can also overlap with each other. Hence, there exists a bonding interaction among one of

the 3d orbital of the chlorine or phosphor atom, one of the 3d orbital of the metal atom, and the 2p_z orbital of the α-carbon atom. This bonding interaction stabilizes the electron in 2p_z orbital of the α-carbon atom in some degree. Thus, the reaction barriers of the reactions **9** and **10** are lowered (125.0, 125.6 kJ·mol^{-1}).

On the contrary, when R_4 is a methyl group （or a CF_3 group), the four sp^3 hybrid orbitals of the carbon atom in R_4 position are used to form four σ bonds with three hydrogen （or flourine) atoms and one metal atom, no orbital left to overlap with the 3d orbital of the metal, implying that a methyl group （or a CF_3 group) in position R_4 cannot stabilize the electron in the p_z orbital of the α-carbon atom through the orbital interaction. Therefore, the reaction barrier is high (133.8 and 132.1 kJ·mol^{-1}) for the reactions **4** and **7**.

For the reaction **8** where R_4 is a fluorine atom, the fluorine atom has three no bonded 2p orbitals, one of them can interact with the 3d orbital of the metal atom forming a π bonding orbital. However, on account of the big difference between the energies of the two orbital levels, there exists little effective bonding. Hence, the reaction barrier is high (132.1 kJ·mol^{-1}).

It can be reasonably deduced that if both R_3 and R_4 are PH$_2$ groups, the reaction barrier should be even lower than that of the reaction **10** where R_4 is a PH$_2$ group and R_3 is a methyl group. The reaction **11** was therefore designed to check this guess. The calculation results about the reaction **11** are in Table 1. The data in Table 1 show that the reaction barrier of the reaction **11**, where both R_3 and R_4 are PH$_2$ groups, is 122.5 kJ·mol^{-1}, 3.1 kJ·mol^{-1} lower than that of the reaction **10**, where one is a PH$_2$ group and another one is a methyl group (125.6 kJ·mol^{-1}). Table 1 shows that the first PH$_2$ group decreases the barrier from 133.8 to 125.6 kJ·mol^{-1}, the second PH$_2$ group decreases the barrier from 125.6 to 122.5 kJ·mol^{-1} (the reactions **4**, **10** and **11**).

Our calculations show that the most favorable group for R_1 or R_2 is the methyl group, the most favorable group for R_3 or R_4 is the PH$_3$ group. Therefore, it can be reasonably deduced that both R_1 and R_2 are methyl groups and both R_3 and R_4 are PH$_2$ groups will decrease the reaction barrier substantially. In order to

check this deduction, we designed the reaction **12**. The data in Table 1 show that the reaction barrier of the reaction **12** is only 89. 7kJ·mol^{-1}.

Since the 3*d* orbital of the silicon or chlorine atom has almost the same orbital energy level as the 3*d* orbital of the phosphor of PH$_2$ group, the silyl group or chlorine atom should have the same effect on the reaction barrier as a PH$_2$ group. We carried out calculations on the reactions **13** and **14** and found that the reaction barriers of the reactions **13** and **14** are 89.4 and 87.8 kJ·mol^{-1}, respectively, almost the same as that of the reaction **12**. These calculation results support the idea that the orbital interactions play an important role in the intramolecular α-hydrogen transfer reactions.

3　Summary

In a summary, it is found that in all fourteen transition states studied in this paper the sp^2 hybridization has been adopted by the central α-carbon atom, from which the hydrogen atom has shifted. The reaction barrier will be lowered by the substituents that delocalize the unpair electron in the unhybridized p_z orbital of the central α-carbon atom. The most preferable substituent is the methyl group for R$_1$ and/or R$_2$. For R$_3$ and R$_4$, the PH$_2$ group or Silyl group or chlorine atom is a favorite substituent. Both R$_1$ and R$_2$ are methyl groups and both R$_3$ and R$_4$ are PH$_2$ groups or Silyl groups or chlorine atoms will decrease the reaction barrier substantially. Our calculations support the idea that the orbital interactions play an important role in the intramolecular α-hydrogen shift reactions.

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