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A DFT study on the effect of hydrogen bonding on the reaction of a μ-benzoquinone diruthenium complex with acetylene

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ABSTRACT

A DFT study was carried out to investigate the reaction mechanisms of a model μ-benzoquinone diruthenium complex $\{CpRu(\mu\text{-}H)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_4O_2)$, derived from the experimental compound $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_3RO_2)$ (R = H or R = Me, $Cp^* = \eta^5\text{-}C_5Me_5$), with acetylene both in aprotic and protic solvents. Results of calculations show that the influence of the solvent methanol on the reaction is mainly on the step of acetylene coordination. Enhanced hydrogen bonding is the reason for acceleration of the reaction in protic solvent, which is supported by NBO charge analysis.

1. Introduction

Transition metal polyhydride complexes [1–4] play an important role on the C–H activation reaction of alkanes [5–8], arenes, alkynes [9,10] and alkenes [11–19]. They also can be used as catalysts for hydrogenation of unsaturated hydrocarbons. It has been well studied on the behaviors of mononuclear polyhydride complexes [9,20–23]. Dinuclear transition metal complexes are more favorable to generate unsaturated sites on the two metal centers, making them likely cooperate for the activation of a substrate. Dinuclear polyhydride complexes have been attracting considerable interests as versatile precursors of the active species for C–H activation of hydrocarbons.

A novel dinuclear tetrahydride-bridged ruthenium complex was synthesized [24] in 1988, which can be used to activate the C–H bond of ethylene [25]. In 2008, Suzuki et al. performed its reaction with 1,4-benzoquinone and 2-methyl-1,4-benzoquinone, respectively, to give the products $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_3RO_2)$ (R = H or R = Me, $Cp^* = \eta^5\text{-}C_5Me_5$) [26]. Such products react with acetylene both in aprotic and protic solvents to yield μ-vinyl-μ-η^2:η^2-1,4-benzoquinone complexes. As experimental results indicated, the reaction rate is more significantly accelerated in protic solvents such as phenol and methanol than in aprotic solvents such as benzene [26].

To our knowledge, theoretical studies on the activation of alkyne by such dinuclear transition metal polyhydrides are little reported [27]. In this work, our goal is to investigate the reaction mechanisms both in protic and aprotic solvents and to explore why the reaction rate is accelerated in protic solvents. We hope this study could provide further understanding for such kind of reactions.

2. Computational details

Molecular geometries of all the complexes studied were optimized at the Becke3LYP level of density functional theory [28–31]. Frequency calculations at the same level of theory were also performed to identify all the stationary points as minima (zero imaginary frequencies) or transition states (one imaginary frequency) and to provide free energies at 298.15 K. The intrinsic reaction coordinate (IRC) analysis was carried out to confirm that all stationary points are smoothly connected to each other. The lanl2dz basis set [32] was used for Ru atoms and the 6-31G [33] basis set was used for other atoms. Polarization functions were selectively added for C, O and H atoms [C(ζ_d = 0.8), O (ζ_d = 0.8) and H(ζ_p = 0.11)], except for those C and H atoms in the two Cp ligands. The natural bond orbital (NBO) program [34], as implemented in GAUSSIAN 03, was also used to obtain natural populations of atoms [35,36]. All the DFT calculations were performed with GAUSSIAN 03 packages [37].

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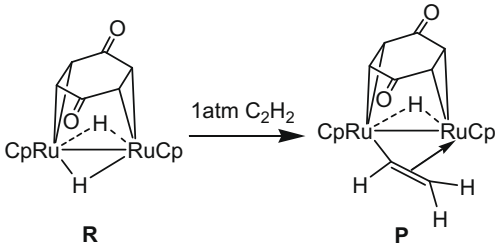
3. Results and discussion



(1)

Solvent: a) benzene, b) methanol.

In this work, the model reaction is shown in Eq. (1). The model reactant $\{CpRu(\mu\text{-}H)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_4O_2)$ (**R**) is derived from the experimental compound $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_3RO_2)$ (R = H or R = Me, $Cp^* = \eta^5\text{-}C_5Me_5$). In other words, Cp^* is modeled by Cp, and R = H in the model reaction. Although replacement of Cp^* by Cp indeed reduces the steric hindrance, the trend for variation of relative energies cannot be changed. As shown in Fig. 1, the computed structural parameters of the model reactant **R** are in well agreement with the X-ray crystalline diffraction data of the experimental compound involving Cp^*, suggesting the B3LYP method used in this work is feasible.

Experimental facts confirmed that the reaction was significantly accelerated in a protic solvent. For example, the reaction rate in methanol was three times faster than in benzene. Suzuki et al. predicted that the accelerated reaction rate is a result of formation of the hydrogen bonding between the oxygen in benzoquinone and the hydrogen of methanol. The first part of this work is to investigate the two reaction mechanisms in aprotic and protic solvents, and the second part aims to explain why the reaction rate is accelerated in protic solvents.

3.1. Reaction mechanisms

The aprotic solvent used in experiment is benzene. Considered the fact that the interaction of benzene with the reactant **R** is very weak, the solvent benzene was not involved in our calculations. The protic solvents used in experiment are phenol and methanol, respectively, and 2.5 phenol molecules were experimentally found to form hydrogen bonds with the reactant **R**. In our model reaction, only one methanol molecule was employed for the purpose of investigating the influence of the protic solvent on the reaction rate. All the transition metal complexes involved in this study are schematized in Fig. 1, with selected structural data. The calculated free energy profile for formation of the product **P** by reaction of the dinuclear reactant **R** with acetylene is shown in Fig. 2, where the influence of the solvent, benzene, is not considered. The calculated free energy profile for formation of the product **P′** by reaction of the dinuclear reactant **R′** with acetylene is shown in Fig. 3, in which the protic solvent, methanol, is involved.

As shown in Fig. 2, two steps are involved. The first step is the coordination of acetylene to one metal center of the dinuclear complex **R** to give an acetylene complex (**Int1**). The hydride H1 gradually moves to Ru2 (see Fig. 1). The free activation energy is calculated to be 25.8 kcal/mol, mainly arising from breaking of Ru1–H1 bond and weakening of Ru1–Ru2 bond (2.74 Å in **R** and 3.04 Å in **TS1**). **Int1** is less stable than **R** by 18.0 kcal/mol in free energy, mainly resulting from the cleavage of Ru1–H1 and decreased Ru1–Ru2 bond strength. The second step is the transfer of the hydride H1 to C4 of acetylene from Ru2. The calculated free activation energy is only 8.1 kcal/mol indicating the hydride transfer is facile kinetically. The free energy difference for this step is −43.7 kcal/mol and that for the overall reaction is −25.7 kcal/mol, confirming the product is very stable. The high stability of **P** is due to formation of stable C4–H1 σ-bond and the occurrence of the C3=C4 π-bond coordination to Ru2. The calculated bond distances of Ru2–C3 (2.23 Å) and Ru2–C4 (2.33 Å) confirmed the binding between Ru2 and C3=C4.

Fig. 3 shows the reaction mechanism involving the influence of the solvent, methanol. This mechanism is similar to the one shown in Fig. 2, in addition to the involvement of methanol. In all the species shown in Fig. 3, the solvent methanol forms a hydrogen bond with one of the quinonoid oxygen atoms. Comparing the two Figs. 2 and 3, one can see the free activation energies in the second step are similar (8.1 and 8.6 kcal/mol), suggesting the solvent methanol has little influence on the hydride transfer from metal center to acetylene. However, the influence of the solvent on the first step is noticeable. The free energy difference for the first step in Fig. 2 (18.0 kcal/mol) is markedly higher than the one in Fig. 3 (14.1 kcal/mol), suggesting the acetylene coordination is more thermodynamically favorable as a result of the occurrence of the hydrogen bonding. The free activation energy for acetylene coordination to Ru1 is also apparently reduced as the protic solvent methanol is considered (from 25.8 kcal/mol in Fig. 2 to 21.5 kcal/mol in Fig. 3), which is well in accordance with the experimental observations that the reaction was accelerated in protic solvents. We concluded from above analysis that the protic solvent mainly imposes influences on the acetylene coordination to the metal center.

3.2. Discussion on the two reaction mechanisms

On the basis of the conclusion obtained above, we mainly discuss the influence of protic solvent methanol on the acetylene coordination to metal center (the first step). The NBO charges calculated for selected species are listed in Table 1.

Let us first talk about the influence of methanol on the reactant **R**. Clearly, methanol forms a hydrogen bond with **R** to afford **R′**. The hydrogen bond distance of O1···H2 is calculated to be 1.86 Å. It is found the hydrogen bonding can induce the back donation of d electrons in Ru centers to the π^* orbital of benzoquinone to a higher extent, which can be qualitatively elucidated from the relative energies of their π^* of benzoquinone. For comparison, we respectively calculated the energy of the π^* of the fragment benzoquinone directly derived from **R**, and that of the fragment methanol···benzoquinone from **R′**. Calculated results show that the former (−0.05127 au) is higher in energy than the latter (−0.05664 au), suggesting electron transfer from Ru to the π^* of benzoquinone is enhanced as a result of the hydrogen bonding between methanol and benzoquinone.

As shown in Table 1, the NBO charges on C1 and C2 bound to Ru1 increase from **R** to **R′**. As a result of inductive effect, the electron density on the oxygen atoms of benzoquinone correspondingly increases. As calculated, the NBO charges on O1 increase from **R** to **R′** (from −0.5543 to −0.6043). To further support the issue, we optimized the geometric structure in which methanol simply interacts with benzoquinone. The calculated NBO charge on oxygen of H···O is −0.5200, smaller than that in **R′**. Correspondingly, the H···O distance (1.94 Å) is longer than that in **R′**. This provides circumstantial evidence for the enhanced hydrogen bonding in **R′** due to the involvement of transition metal centers.

Clearly, the electron density on metal centers decreases from **R** to **R′**. As shown in Table 1, the NBO charges on Ru1 in **R** and **R′** are −0.3051 and −0.2706, respectively. As a result, acetylene that mainly acts as a σ-donor becomes easier to attack **R′** rather than **R**.

Let us move to the comparison of the first step shown in Figs. 2 and 3. To probe why ethyne coordination is more facile in methanol than in benzene as shown in Figs. 2 and 3, a simple energy-decomposition

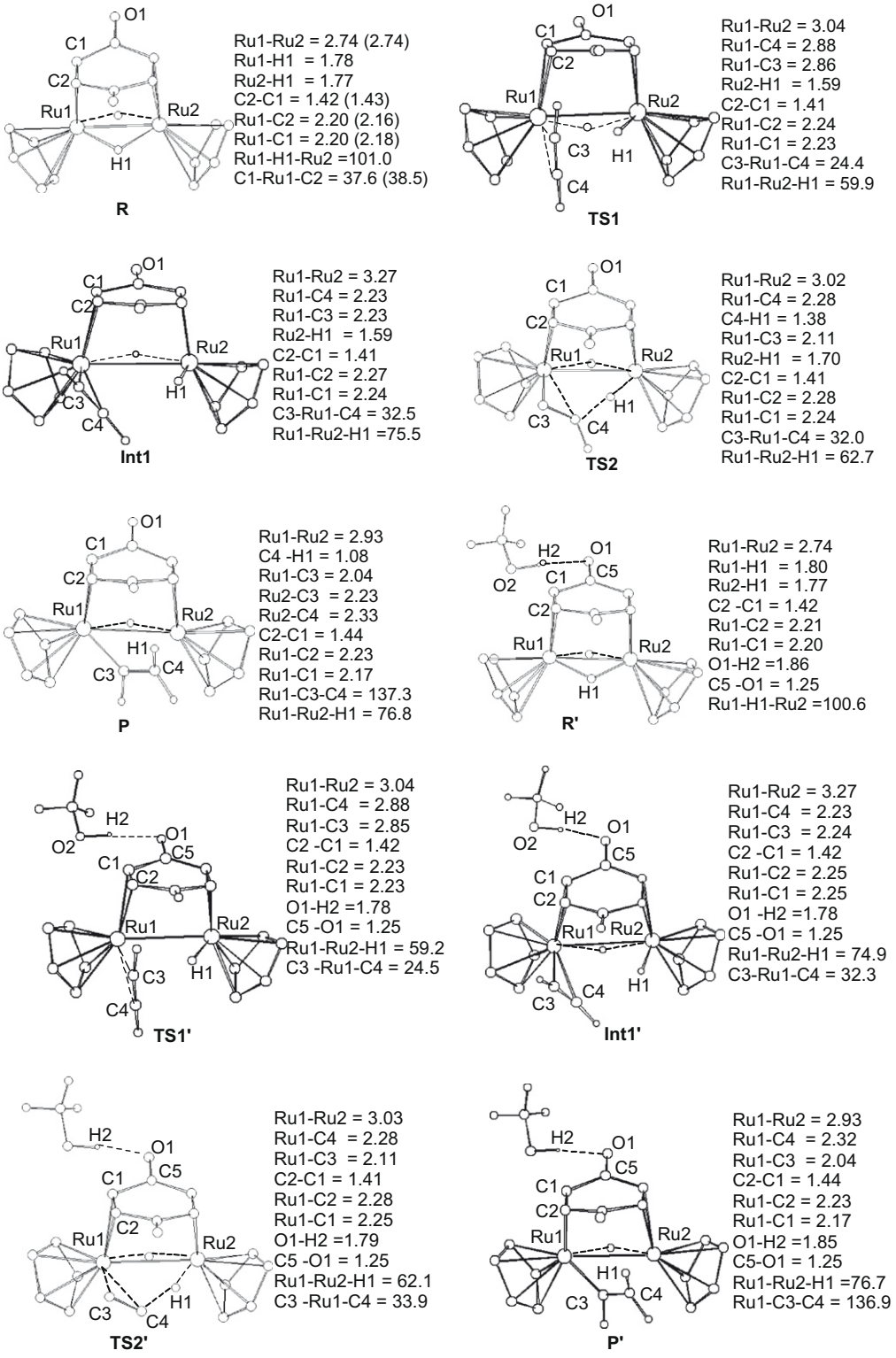


Fig. 1. Selected B3LYP optimized structures involved in the model reaction together with selected bond distances and bond angles. The bond distances are given in Å. In **R**, the X-ray crystalline diffraction data of the original compound involving Cp* are given in parenthesis.

analysis (EDA) [38–40] is carried out as illustrated in Scheme 1. **f** from **R-f1**, **R-f2** and so on represents a fragment. The fragments on the left side are directly derived from the compounds on the right side. ΔE_1, ΔE_2, $\Delta E_1'$ and $\Delta E_2'$ represent the binding energy of each pair of two fragments. Clearly, due to existence of hydrogen bonding between the methanol hydrogen and the quinonoid oxygen, the binding between the two fragments, benzoquinone and $[CpRuH]_2$, is enhanced by 3.9 kcal/mol as shown in Scheme 1a. The enhanced binding between the two fragments in **R′** is resulted from the stronger back bonding from the metal center to the π^* of benzoquinone, which is in accordance with the variation of NBO charges on Ru, C1 and C2 as mentioned above.

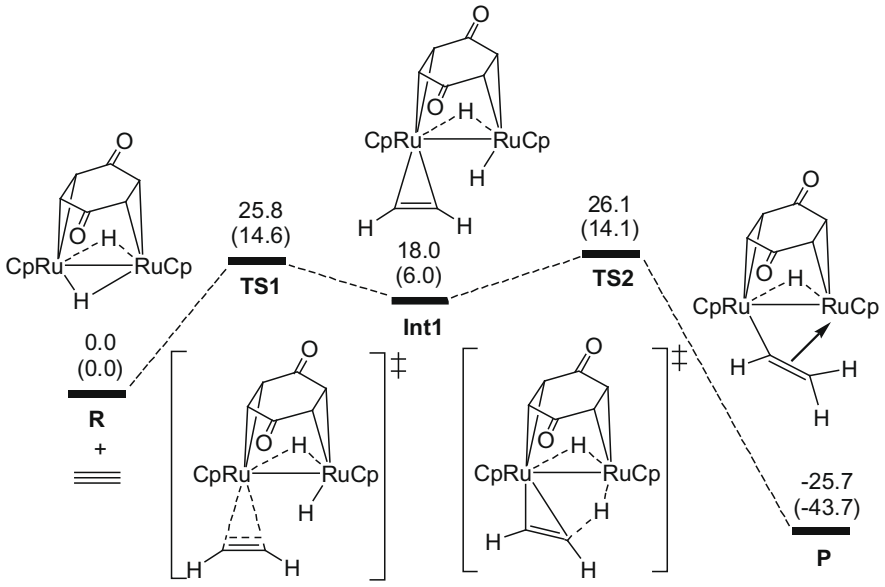


Fig. 2. Free energy profile calculated for the model reaction (1) without considering the influence of the protic solvent. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

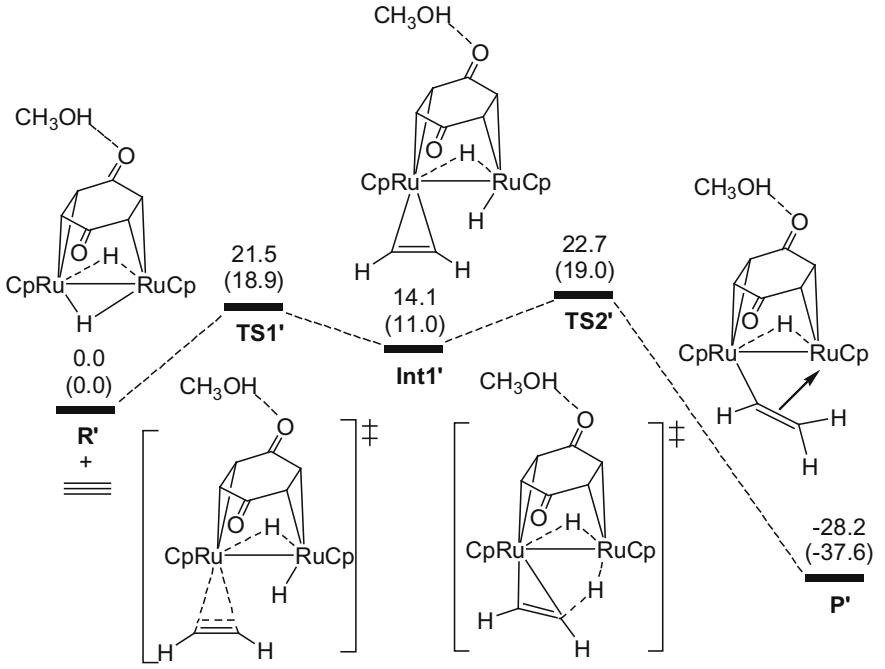


Fig. 3. Free energy profile calculated for the model reaction (1) involving the influence of the protic solvent. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

As shown in Scheme 1b, the binding energy in **Int1**′ ($\Delta E_2'$) is also higher than that in **Int1** (ΔE_2). It is worth to note that the increased value of the binding energy from **Int1** to **Int1**′ (8.3 kcal/mol) is higher than that from **R** to **R**′ (3.9 kcal/mol). This qualitatively predicts that the energy difference from **R**′ to **Int1**′ is smaller than that from **R** to **Int1**, which is in agreement with our results of calculations as shown in Figs. 2 and 3.

Why is the barrier from **R**′ to **TS1**′ lower than that from **R** to **TS1**? This can be interpreted in terms of the relative hydrogen bonding strength formed in **R**′ and **TS1**′. From Fig. 1, it can be seen that the hydrogen bond distances in **R**′ and **TS1**′ are 1.86 and 1.78 Å, which is in accordance with the NBO charges on the oxygen (O1: −0.6043 in **R**′ and −0.6166 in **TS1**′). This confirmed that the hydrogen bonding in **TS1**′ is stronger than that in **R**′ (−12.1 kcal/mol in **R**′ and −14.0 kcal/mol in **TS1**′). In other words, the solvent methanol stabilizes **TS1**′ to higher extent relative to **R**′. In summary, as acetylene attacks the metal center, enhanced back donation from Ru to the π^* orbital of benzoquinone enables the quinonoid oxygen atoms electron-richer from **R**′ to **TS1**′, leading to a smaller barrier compared to the one from **R** to **TS1**. Therefore, the reaction rate for the μ-benzoquinone diruthenium complex with ethyne in methanol is greater than that in aprotic solvent,

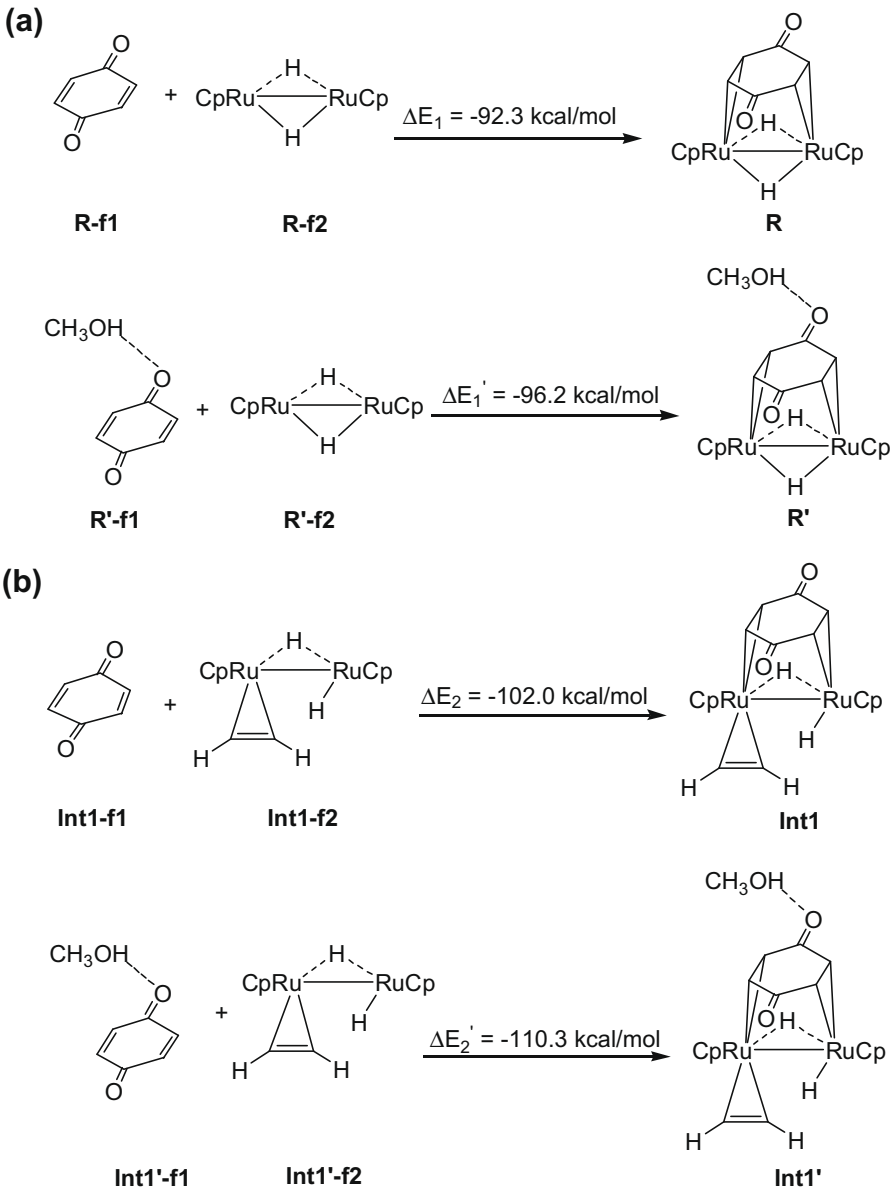
Table 1
Selected NBO charges calculated for the species involved in the first step in Figs. 2 and 3.

R	TS1	Int1
Ru1 = −0.3051	Ru1 = −0.1099	Ru1 = −0.2831
C2 = −0.2986	C2 = −0.3208	C2 = −0.2934
C1 = −0.2981	C1 = −0.2653	C1 = −0.2651
O1 = −0.5543	O1 = −0.5638	O1 = −0.5721
	C4 = −0.2315	C4 = −0.1772
	C3 = −0.1851	C3 = −0.1759
R′	**TS1′**	**Int1′**
Ru1 = −0.2706	Ru1 = −0.1017	Ru1 = −0.2872
C2 = −0.3015	C2 = −0.3258	C2 = −0.2976
C1 = −0.3011	C1 = −0.2716	C1 = −0.2736
O1 = −0.6043	O1 = −0.6166	O1 = −0.6157
H2 = −0.4951	H2 = −0.4980	H2 = −0.4971
O2 = −0.8047	O2 = −0.8121	O2 = −0.8084
	C4 = −0.2298	C4 = −0.1779
	C3 = −0.1858	C3 = −0.1759

which is in accordance with the experimental observations that "the reaction rate in methanol was three times faster than in benzene" [26].

In addition, the ligand acetylene is found to mainly act as a σ-donor on the basis of the calculated NBO charges. The calculated NBO charges on the two carbon atoms of acetylene for free acetylene, **TS1′** and **Int1′** are (−0.2439, −0.2439), (−0.2298, −0.1858) and (−0.1779, −0.1759), respectively. That means as acetylene attacks Ru center via **TS1′** to give **Int1′**, the NBO charges on the two carbon atoms of acetylene obviously decrease. So the σ-donation is predominant rather than the π-acception between acetylene and the metal center.

In this study, we employed only one methanol molecule that forms a hydrogen bond with the oxygen of benzoquinone. We have also computed the data for the case involving two methanol molecules. The second methanol molecule forms a hydrogen bond with the other quinonoid oxygen. The free energies of the corresponding transition state and the intermediate for the first step



Scheme 1.

(coordination of acetylene) are calculated to be 20.3 and 13.8 kcal/mol, respectively. The values are lower than those corresponding to the case involving one methanol molecule (**TS1′**: 21.5 kcal/mol, **Int1′**: 14.1 kcal/mol). It can be certainly predicted, multiple hydrogen bonding would actually lead to better agreement with the experimental data.

4. Conclusions

The reaction mechanisms of a model μ-benzoquinone diruthenium complex $\{CpRu(\mu\text{-}H)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_4O_2)$, derived from the experimental compound $\{Cp^*Ru(\mu\text{-}H)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_3RO_2)$ (R = H or R = Me, $Cp^* = \eta^5\text{-}C_5Me_5$), with acetylene both in aprotic and protic solvents have been investigated through DFT calculations. The first step is the acetylene coordination to the Ru center, and the other is the hydride transfer from Ru center to acetylene. It is found that the influence of methanol on the reaction is mainly on the barrier of the first step. Hydrogen bonding involved in the dinuclear polyhydride reactant results in the increase of acidity of Ru, enabling acetylene more facile to attack Ru center. The enhancement of hydrogen bonding from **R′** to **TS1′** leads to a smaller barrier for the step relative to the barrier from **R** to **TS1**.

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