

Article

The Pincer Ligand Supported Ruthenium Catalysts for Acetylene Hydrochlorination: Molecular Mechanisms from Theoretical Insights

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Abstract: Pincer ligand supported Ru^{II} chloride complexes may be used for acetylene hydrochlorination as non-mercury molecular catalysts. Based on theoretical calculations, the catalytic mechanism and the interaction between catalysts and reactants has been evaluated, indicating that the (pincer)Ru^{II}Cl₂ platform supports electrophilic proton-ruthenation of C₂H₂. Energy decomposition studies further illustrate the electron-rich property of the Ru^{II} center, which can increase the negative charge of C₂H₂ via 4d-electron backdonation. Thus, the electrophilic reaction mechanism is favored due to lower energetic barriers. By improving the electron-donating ability of ligands, this lowering of energetic barriers can be enhanced. Therefore, non-mercury catalysts for acetylene hydrochlorination with milder reaction conditions and higher catalytic activity can be designed.

Keywords: acetylene hydrochlorination; reaction mechanism; ruthenium complex molecular catalyst; DFT calculations



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1. Introduction

Vinyl chloride monomer (VCM) is the major chemical intermediate leading to polyvinyl chloride (PVC), which is one of the most important polymers in use today with the production of over 40 million tons annually [1,2]. For industrial VCM production, acetylene hydrochlorination has been widely applied in countries where acetylene can be obtained economically from coal, using mercuric chloride (HgCl₂) supported on activated carbon as the industrial heterogeneous catalyst [3,4]. However, the mercury-based catalyst has a number of serious problems, namely the facile volatility of mercuric chloride under the reaction temperature (170–180 °C), which results in mercury loss leading to deactivation of the catalyst and environmental poisoning. Moreover, the use of mercury-based catalysts will be forbidden by the Minamata Convention [5]. With the concerns associated with the severe mercury loss from the industrial units, it is necessary to produce a new, non-mercury heterogeneous catalyst for the acetylene hydrochlorination process. Over the past few decades, the catalytic performance of various metal chlorides for use in this reaction has been systematically investigated [6,7].

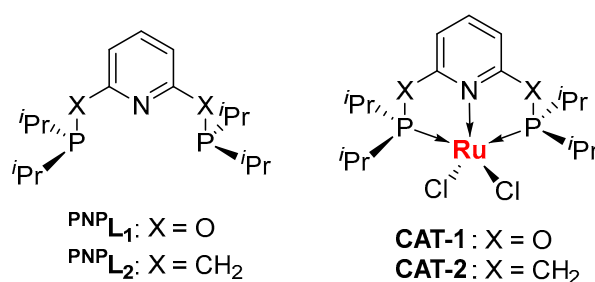
The Hutchings group have conducted pioneer work showing the possibility of a gold-based non-mercury commercial catalyst. They showed that the initial activity in catalytic acetylene hydrochlorination may be related to the standard reduction potential of metal cations [7]. It is observed that the potential of a gold-based catalyst leads to a well-performing catalyst. Up to now, their industrial gold-based catalyst has shown good performance in activity and stability [3,8]. However, as gold is one of the noble metals, there is interest in finding low-cost metals which have similar performance. Late-transition metals, such as group VIII, IB, and IIB metal compounds, are also expected to

be effective catalysts. Among these compounds, recent studies have mainly focused on copper, ruthenium, and palladium as a single-metal catalyst [9,10].

Unlike the mercury loss that mainly leads to catalyst deactivation, non-mercury catalysts may undergo coke deposition or metal species agglutination (sintering) causing activity loss. The coke deposition phenomenon of non-mercury catalysts is thought to cause the acetylene polymerization-dehydrogenation process, with more acidic catalysts leading to a greater effect. On the other hand, the active metal ions may be reduced by acetylene and aggregate at the reaction temperature [3,11]. According to the existing research, there are two main ways to improve catalytic performance, and avoid sintering and coke deposition. Promoting the conversion from acetylene to VCM may effectively prevent the self-polymerization of acetylene. This is generally achieved by enhancing the adsorption and activation of hydrogen chloride on heterogeneous catalysts. The presence of support ligands is crucial for improving the stability of the metal ions and avoiding side reactions on the metal center. In addition, careful construction of the ligand support may improve the metal dispersion and prevent sintering [12].

The development of non-mercury catalysts for acetylene hydrochlorination is thus focused on engineering the supporting ligands through additive-based modification and generation of novel metal complexes. The support designing and modification aims to increase the electronic density, which is beneficial for the stronger metal-support interaction and the adsorption of HCl [12,13]. Importantly, if the additive or support is able to bind to the metal center as a ligand, the metal complex will be generated as a molecular system and the species can be highly dispersed on the support. For transition metal chlorides, the excess chloride anions were confirmed to be able to coordinate with metal centers, which may tune the catalytic performance for acetylene hydrochlorination, such as $[\text{PtCl}_4]^{2-}$, $[\text{PtCl}_6]^{2-}$, $[\text{PdCl}_4]^{2-}$, $[\text{AuCl}_4]^{-}$, $[\text{RuCl}_4]^{-}$, $[\text{CuCl}_x]^{1-x}$ ($x = 2, 3$ or 4) [14–22]. In addition to the Cl^{-} anion, some organic and inorganic ligands have received increasing attention recently. $\text{S}_2\text{O}_3^{2-}$ and $\text{SC}(\text{NH}_2)_2$, etc. are used for Au [3,4], N-alkylpyrrolidone (amides), amines, pyridines are used for Cu or Ru, where Ru allows wider applicability to neutral nitrogen-containing ligands, including azoles, guanidines, and N-heterocyclic carbenes [23–32]. The formation of these metal complexes allow for the depolymerization of the metal center from the metal chlorides cluster, and if the electronic effects and steric hindrance of the ligand are suitable, molecular complexes may be obtained allowing another avenue of exploration of “single-site” catalysts [33].

For this study, the ruthenium-based catalyst is investigated for its potential for high-performance-catalysis suggested by Kang et al. [34]. Beyond ruthenium trichloride RuCl_3 , the organometallic ruthenium catalysts may have a lower Lewis acidity that benefits acetylene hydrochlorination. Dérien et al. have reported the homogeneous hydrochlorination of substituted alkynes catalyzed by a Ru^{II} -complex supported by the pentamethylcyclopentadiene anion (Cp^*) and phosphorus ligands at room temperature, showing a highly efficient method with wide applications in organic synthesis [35]. The mechanistic studies suggest that the Ru^{II} center shows π -backdonation to alkynes, which allows the electrophilic addition by HCl with a low energy barrier [36]. Alternatively, we would like to consider a neutral ligand here, rather than an ionic ligand like cyclopentadiene anion, to discuss the enhancement of ruthenium chloride catalysts. Phosphorus ligands are well matched for the group VIII metals, and the additional chelation effect enhances the stability of the complexes. In this work, the PNP pincer ligands $^{\text{PNP}}\text{L}_1$ and $^{\text{PNP}}\text{L}_2$ were considered for the generation of Ru^{II} -chloride complexes (Scheme 1).



Scheme 1. The pincer ligands used to modify the ruthenium(II) chloride as the catalysts for acetylene hydrochlorination. $i\text{Pr} = \text{CH}(\text{CH}_3)_2$ (isopropyl).

2. Results and Discussions

Complex $(^{\text{PNP}}\text{L}_1)\text{RuCl}_2$ (**CAT-1**) and $(^{\text{PNP}}\text{L}_2)\text{RuCl}_2$ (**CAT-2**) were selected for investigating the catalytic mechanism of acetylene hydrochlorination. The mechanism was discussed in Section 2.1 *The interaction between catalysts and reactants* and Section 2.2 *The Gibbs free energy of intermediates and transition states*.

2.1. The Interaction between Catalysts and Reactants

The optimized structures of the complex $(^{\text{PNP}}\text{L}_1)\text{RuCl}_2$ (**CAT-1**) and $(^{\text{PNP}}\text{L}_2)\text{RuCl}_2$ (**CAT-2**) show a quadrilateral cone coordination with a vacant ligand site as the active site. The most stable structures of the complexes interacting with C_2H_2 or HCl separately are presented in Figure 1. The adsorption Gibbs free energy (ΔG_{ads}) of HCl on **CAT-1** and **CAT-2** are +0.90 and -3.64 kcal/mol, respectively. While ΔG_{ads} of C_2H_2 adsorbed on **CAT-1** and **CAT-2** are -11.53 and -9.89 kcal/mol, respectively (Table 1). Thus, the adsorption of C_2H_2 by catalysts is more favored than HCl , which is consistent with previous studies [3,12,18,19]. The HCl adsorption capacity of **CAT-2** is larger than **CAT-1** due to its more negative ΔG_{ads} . Note that the basis-set superposition error (BSSE) under the counterpoise treatment should be included for calculating the adsorption Gibbs free energy between catalysts and reactants. In the interacting structure, an HCl molecule coordinates its Cl atom to the Ru^{II} center. Meanwhile, the H atom of HCl is attracted by the Cl^- anion of the catalyst via hydrogen bonding. These effects lead to the significant increase of the H-Cl bond length (~ 1.38 Å for HCl on **CAT-1** and ~ 1.37 Å for HCl on **CAT-2**) compared to a free HCl (~ 1.29 Å). However, the Hirshfeld charge of HCl on **CAT-1** and **CAT-2** are -0.03 and -0.015 , respectively. It implies that the catalyst does not donate electrons to activate HCl . Therefore, the metal- Cl (Cl in HCl) coordination is counterbalanced by the complex- H (H in HCl) coordination. This is consistent with the independent gradient model (IGM) analysis results (Figure 2), that the strong attraction was located in the blue area.

Table 1. The adsorption Gibbs free energy (ΔG_{ads}) of HCl and C_2H_2 adsorbed on catalyst **CAT-1** and **CAT-2**.

Adsorption Free Energy ΔG_{ads}^1 /(kcal/mol)	C_2H_2	HCl
CAT-1	-11.53	0.90
CAT-2	-9.89	-3.64

¹ $\Delta G_{\text{ads}} = G_{\text{CAT} + \text{Reactant}} - G_{\text{CAT}} - G_{\text{Reactant}}$. Counterpoise corrections were considered for basis-set superposition errors (BSSE) here.

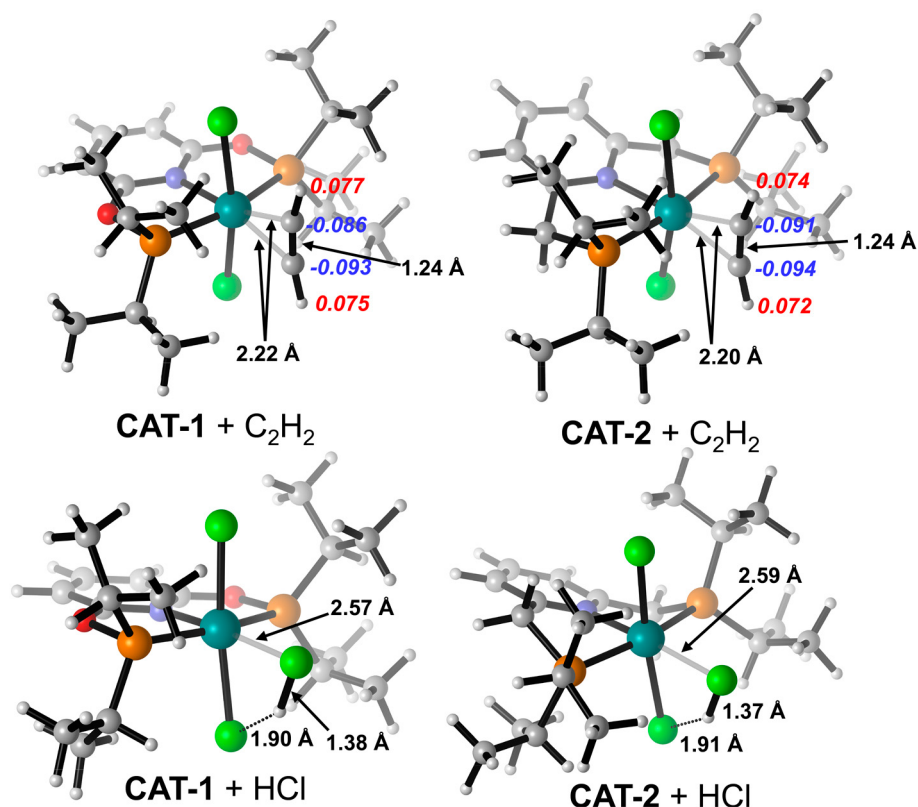


Figure 1. Optimized structures for HCl and C_2H_2 adsorbed by CAT-1 and CAT-2. Key bond lengths (black numbers) and Hirshfeld charges of C_2H_2 (red and blue numbers in *italic font*) were labeled. Ball colors: green (Cl), gray (C), white (H), blue (N), red (O), orange (P), cyan (Ru).

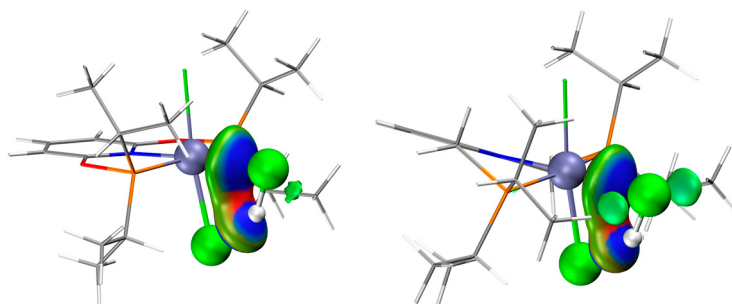


Figure 2. IGM analysis of HCl adsorbed by CAT-1 (left) and CAT-2 (right). Ball colors: green (Cl), gray (C), white (H), blue (N), red (O), brown (P), cyan (Ru). Blue surface represents larger gradient value.

As for C_2H_2 adsorbed on CAT-1 and CAT-2, the attraction is dominated by π -interactions. C_2H_2 can coordinate its π -electrons to the metal center as a Lewis acid. Consequently, the electron density on C_2H_2 is reduced and C_2H_2 is more favored for nucleophilic attacks [37]. Indeed, C_2H_2 can be activated by CAT-1 and CAT-2 as its C-C bond is elongated slightly from 1.21 to 1.24 Å. It is noticeable that the Hirshfeld charge of C_2H_2 is remarkably negative as -0.027 for CAT-1 and -0.039 for CAT-2, respectively. The negative charges are populated on the C atoms of C_2H_2 . This implies that the backdonation from Ru^{II} to C_2H_2 is superior in magnitude compared with the π -coordination of C_2H_2 to Ru^{II} . This will be further discussed in the following reaction mechanism section.

For the co-adsorption of C_2H_2 and HCl, possible interactions are discussed here, which are directly related to the subsequent reaction mechanism. We have found three stable

adsorption minima in total, which correspond to the sequential adsorption of C_2H_2 and HCl . **CAT-1** was taken as an example to illustrate. Figure 3 shows optimized structures and interacting energies with or without BSSE correction. The energies of the structures in the mechanism discussion below, including **INT1**, **INT2** and **INT3** in Figure 3, did not include BSSE. When C_2H_2 binds to the Ru^{II} center first, there are two adsorption sites for HCl , both of which are achieved by attracting the H atom of HCl via hydrogen bonding. Not only the Cl^- anion of **CAT-1** (in **INT1**, $\Delta G = -20.4$ kcal/mol and $\Delta G_{ads} = -12.8$ kcal/mol), but also the π -bond of C_2H_2 (in **INT2**, $\Delta G = -15.0$ kcal/mol and $\Delta G_{ads} = -5.6$ kcal/mol) is able to act as the hydrogen bond acceptor. If HCl binds to the metal center first, C_2H_2 can only find one stable adsorption site. Meanwhile, the π -bond of C_2H_2 interacts with the H atom of HCl via hydrogen bonding (**INT3**, $\Delta G = -4.7$ kcal/mol and $\Delta G_{ads} = 2.6$ kcal/mol), which could be also visualized by IGM analysis (Figure 3b). Interestingly, the H atom of C_2H_2 can form another weak hydrogen bond with the Cl atom of HCl in **INT1**. In the co-adsorption, the structures contain $C_2H_2-Ru^{II}$ coordination is more favorable in energy, which is consistent with the larger ΔG_{ads} of individual C_2H_2 . As for **CAT-2**, a similar conclusion has been found.

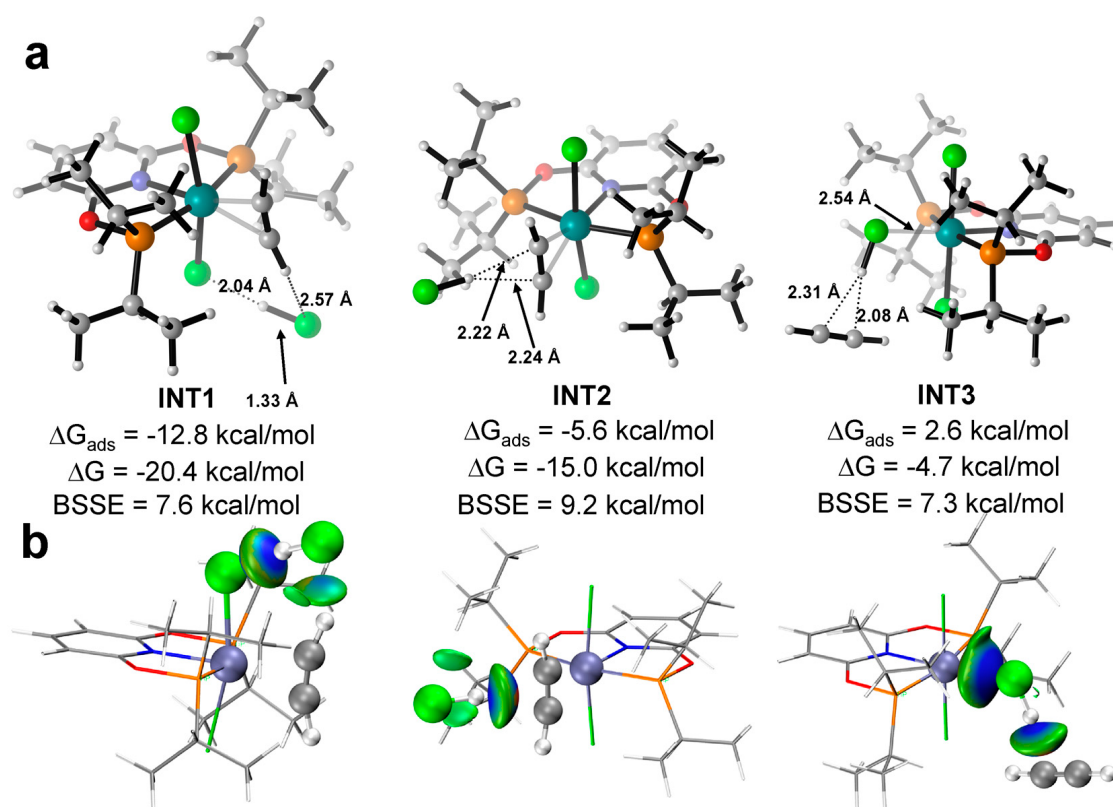


Figure 3. (a) The optimized structure of the co-adsorption state as **INT1**, **INT2** and **INT3** with the key bond length (black numbers); (b) The IGM analysis of **INT1**, **INT2** and **INT3**. Ball colors: green (Cl), gray (C), white (H), blue (N), red (O), brown (P), cyan (Ru).

2.2. The Gibbs Free Energy of Intermediates and Transition States

The pathway-1 of **CAT-1** catalyzed acetylene hydrochlorination is shown in Figure 4. Firstly, we choose **INT1** as the initial adsorption intermediate to investigate possible reaction pathways as **INT1** is the dominating intermediate due to its strongest adsorption. In general, the activation by metal complexes of unsaturated hydrocarbons with respect to the nucleophilic attack has been theoretically revealed by Prof. Roald Hoffmann [38]. Indeed, we have found the chlororuthenation on the C_2H_2 adsorbed by **CAT-1**. The free energy barrier ($\Delta G^\ddagger$) is quite high from **INT1** to **TS1**, up to 43.3 kcal/mol (42.4 kcal/mol for **CAT-2**). This is significantly higher than the results reported [19,27–29,38]. Then, the

H atom of the original HCl bonds with a Cl^- anion of the catalyst to form another HCl molecule. It induced an oxidation addition on the Ru^{II} center. The H–Cl covalent bond was broken and a ruthenium-hydride (Ru–H) intermediate was formed. With no energy barrier, the $-\text{CH}=\text{CHCl}$ group can be rapidly hydrogenated by Ru–H species to form INT6, where the VCM molecule is adsorbed by CAT–1. Finally, VCM is replaced by another C_2H_2 and HCl pair to form INT1 for the next catalytic cycle. The energy of INT1 (next catalytic cycle) is lower than INT6 (-45.9 kcal/mol vs. -38.7 kcal/mol), which is beneficial for releasing VCM. Note that VCM cannot desorb simultaneously due to its remarkably strong adsorption. Returning CAT–1 will cause an energy increase of 13.2 kcal/mol for the next catalytic cycle. Additionally, we have also considered the chlorination of C_2H_2 to generate *cis*-1,2-dichloroethylene (*Z*- $\text{C}_2\text{H}_2\text{Cl}_2$). As expected, this side reaction is almost impossible for the very high energy barrier ($\Delta G^\ddagger = 58.2$ kcal/mol). This reflects that the metal center is extremely difficult to be reduced. Therefore, we expect it to well avoid the reduction of Ru^{II} and the aggregation of metal particles that causes the deactivation of catalysts in acetylene hydrochlorination.

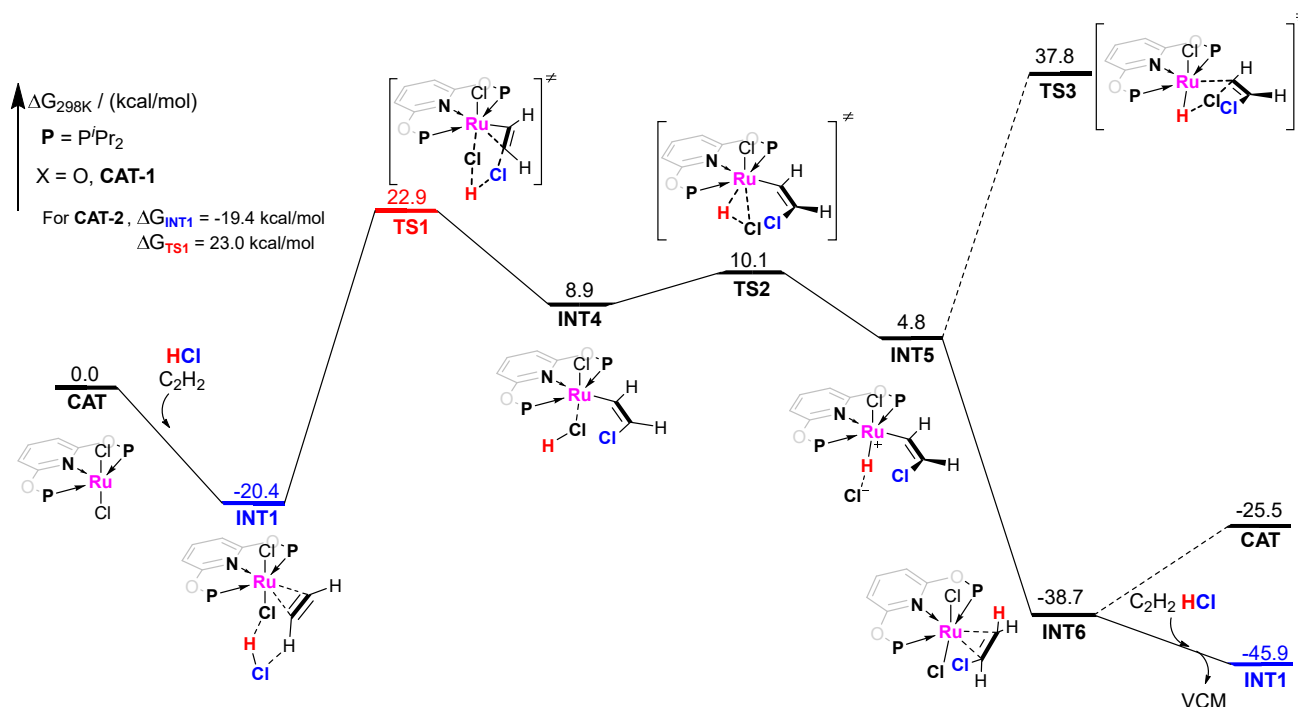


Figure 4. Gibbs free energy profile for molecular complex CAT–1 catalyzed acetylene hydrochlorination mechanism pathway–1.

The pathway–2 of CAT–1 catalyzed acetylene hydrochlorination mechanism is shown in Figure 5. Since the energy barrier of pathway–1 is notably high, we continued to consider INT2 as a slightly less stable adsorption. When C_2H_2 is attached to CAT–1, the π -electrons of C_2H_2 can act as the hydrogen bond acceptor to interact with HCl. Unlike the traditional nucleophilic addition of unsaturated hydrocarbons activated by late transition metal complexes, the proton of HCl adds to the triple bond of C_2H_2 electrophilically via TS4 as the transition state, with an energy barrier of 18.2 kcal/mol. Compared with TS1 in Figure 4, TS4 is the more representative transition state for the electrophilic addition on adsorbed C_2H_2 . The Hirshfeld charge of TS4 can support the electrophilic properties of this step (Figure 5). Interestingly, the potential energy surface of this step is so flat that the energy of intermediate INT7 is very close to that of TS4. In INT7, the C_2H_2 skeleton maintains the three-membered ring connection with the Ru^{II} center. However, the two C atoms in C_2H_2 show a clear difference. The distances of Ru and C^α and C^β are 1.95 and 2.22 Å, respectively. So a more recognizable C–Ru bond is indicated for C^α of C_2H_2 , even

C^β exhibits a similar coordination mode to the adsorbed C_2H_2 initially. The outer-sphere of INT7 is the Cl^- anion, which could transfer the negative charge to C^α to form VCM via TS5 with $\Delta G = 11.9$ kcal/mol. Therefore, $\Delta G^\ddagger$ of the whole pathway–2 is 26.9 kcal/mol. Compared with pathway–1 ($\Delta G^\ddagger = 43.3$ kcal/mol), pathway–2 is more energetically favorable. When CAT–2 is used as the catalyst, $\Delta G^\ddagger$ of the whole CAT–2 catalyzed pathway–2 is much lower, only 17.1 kcal/mol, which illustrates that CAT–2-catalyzed electrophilic addition activity performs much better than CAT–1. The difference between PNP_{L1} and PNP_{L2} is the part attached to the P atom (O atom or $-CH_2-$ group). Considering that the electronegativity of O atom is significantly greater than that of hydrocarbon groups, the electron donating ability of PNP_{L2} is stronger than that of PNP_{L1} . So, this electrophilic proton-ruthenation mechanism is influenced by the electron density of the Ru^{II} center, which can be promoted by the ligands with stronger electron donating ability.

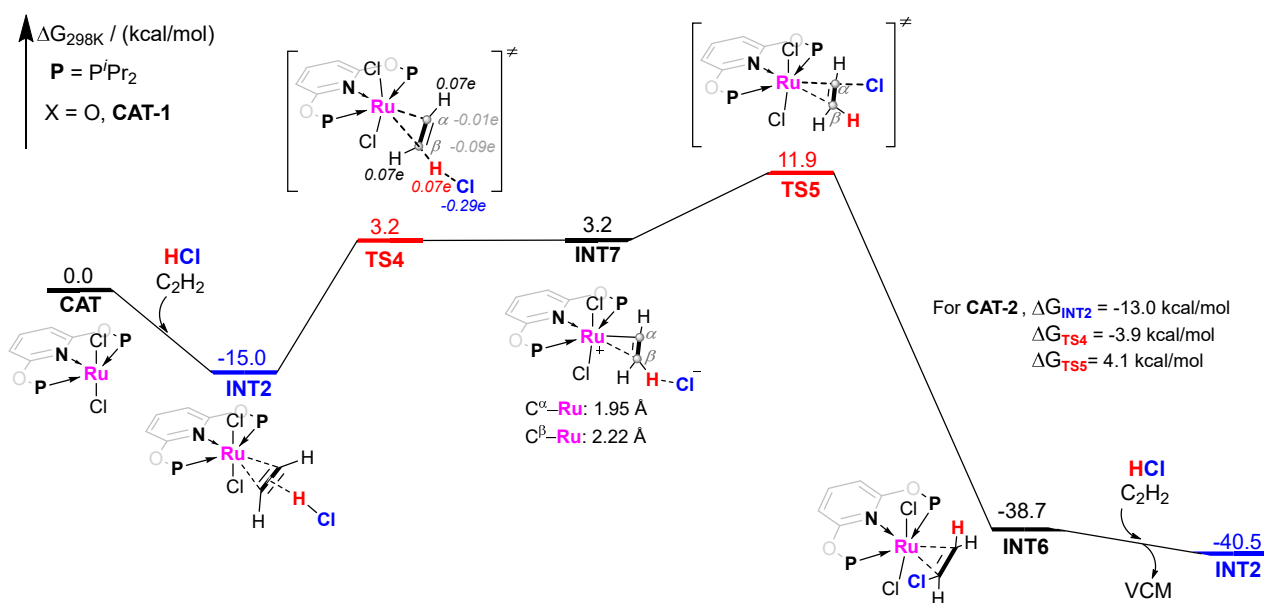


Figure 5. Gibbs free energy profile for molecular complex CAT–1 catalyzed acetylene hydrochlorination mechanism pathway–2. The Hirshfeld charge of important parts was shown in italic fonts.

The viewpoint in pathway–2 may be controversial with the general catalytic mechanism for acetylene hydrochlorination reported in several previous works [19,27–29,38]. However, supporting evidence also exists [39]. In order to give an in-depth understanding, we carried out an energy decomposition analysis (EDA) based on natural orbitals for chemical valence (NOCV) for C_2H_2 adsorbed on the catalyst. In Figure 6, the energy of orbital interaction between C_2H_2 and Ru^{II} can be divided into two parts for CAT–1: the σ -donation from C_2H_2 to Ru^{II} (–16.8 kcal/mol) and the π -backdonation from Ru^{II} to C_2H_2 (–21.3 kcal/mol). It indicates that the backdonation effect is stronger than the coordination effect, which causes more negative charges on C_2H_2 and illustrates a nucleophilic activation. In the total electron deformation density mapping, there is an increased electron density on the backside where C_2H_2 coordinates to Ru^{II} . Thus, C_2H_2 is more susceptible to acidic reagents, e.g., protonic acids, allowing an electrophilic addition mechanism. Additionally, when CAT–2 is used, the σ -donation and the π -backdonation contribute –38.1 and –43.8 kcal/mol to the orbital interaction energy, respectively, revealing the higher activity predicted by a lower energy barrier as studied above.

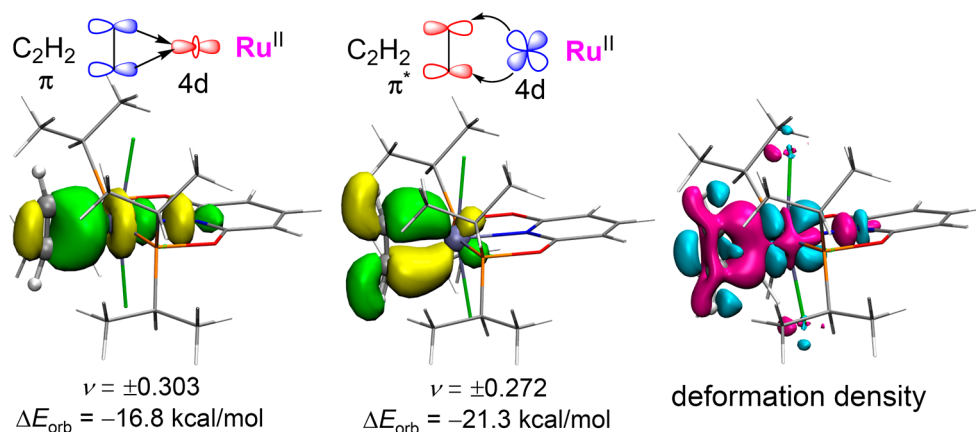


Figure 6. Shape of the charge NOCV orbitals (isovalue = 0.05 a.u.) associated with the orbital interactions ΔE_{orb} and the total electron deformation density for C_2H_2 adsorbed by **CAT-1** (isovalue = 0.0025 a.u.). The eigenvalues (ν) of the fragment orbitals give the size of the charge migration. The color code for the charge transfer is pink $\rightarrow$ cyan.

Moreover, the pathway-3 of **CAT-1** catalyzed acetylene hydrochlorination mechanism is shown in Figure 7. It shows the mechanism started at a relatively unstable adsorption state. A synergistic addition on C_2H_2 was approved in pathway-3. The H atom of HCl and the Cl^- anion of the catalyst adds to the carbon-carbon triple bond simultaneously, which directly leads to the formation of a VCM molecule with $\Delta G^\ddagger$ of 12.9 kcal/mol. Although a lower energy barrier compared with pathway-2 ($\Delta G^\ddagger = 26.9$ kcal/mol) emerged. The adsorption state is not stable enough. **INT8** ($\Delta G = -20.8$ kcal/mol) is prone to adjust its VCM adsorption structure to form a more stable intermediate **INT6** ($\Delta G = -38.7$ kcal/mol), rather than the VCM desorption under HCl and C_2H_2 (-38.7 kcal/mol vs. -30.2 kcal/mol). Similar conclusions were obtained for **CAT-2** ($\Delta G^\ddagger = 14.7$ kcal/mol for pathway-3).

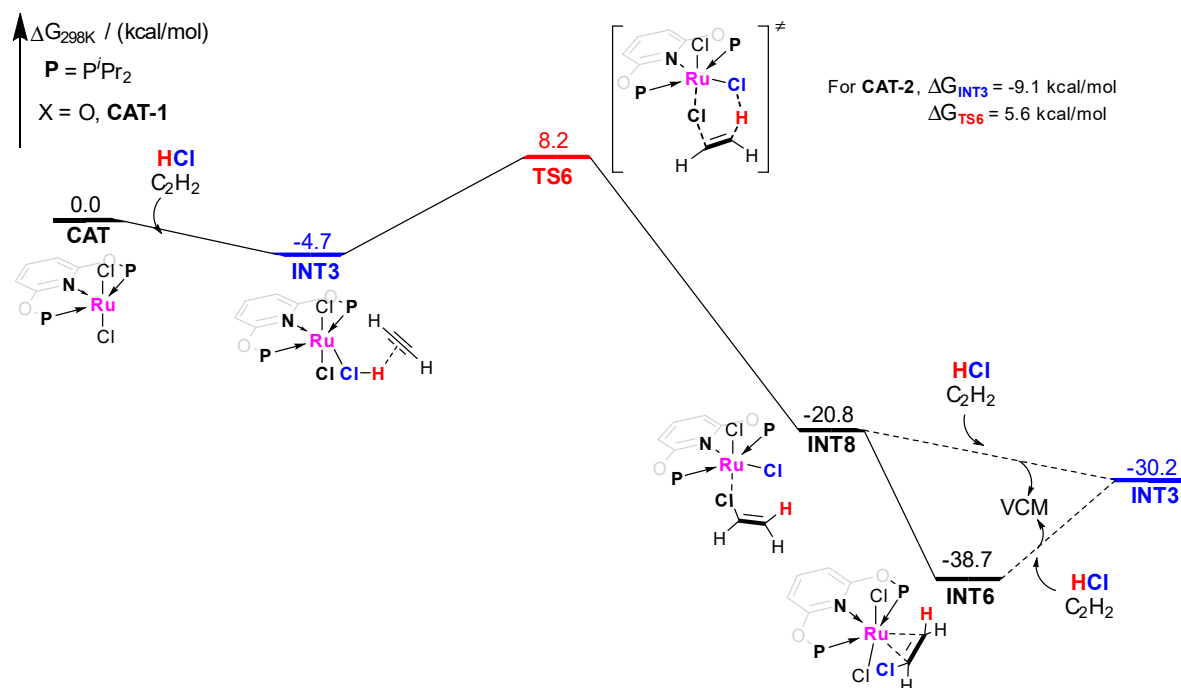


Figure 7. Gibbs free energy profile for molecular complex **CAT-1** catalyzed acetylene hydrochlorination mechanism pathway-3.

To further interpret the mechanistic preference beyond thermodynamic calculations, chemical kinetic evaluations are reported briefly. Figure 8 shows reaction rate constants versus the reaction temperature profile. All the possible intermediates and pathways were considered, including the formation of *cis*-1,2-dichloroethylene ($Z\text{-C}_2\text{H}_2\text{Cl}_2$) as the side reaction. For CAT-1, the rate constant of pathway-3 is the largest despite the relatively unstable adsorption state, indicating that the acetylene hydrochlorination catalyzed by CAT-1 mainly occurs through the synergistic addition of acetylene. The rate constant of pathway-2 is more than two orders of magnitude lower than that of pathway-3. Due to the high energy barrier, the rate constant of pathway-1 is lower, while the rate of side reaction is so slow that it hardly occurs. Compared with CAT-1, rate constants of pathway-2 and pathway-3 catalyzed by CAT-2 are close. Pathway-2, which represents the electrophilic proton-metalation mechanism, plays a dominant role. Additionally, the maximum rate constant in Figure 8b is ~ 10 times that in Figure 8a. So, the Ru^{II} center supported by the stronger electron-donating ligand is the more active catalytic center, and more conducive to the electrophilic proton-metalation mechanism of acetylene hydrochlorination. In summary, we clarified several possible reaction mechanisms based on the thermodynamic calculation. Further chemical kinetic studies evaluated the dominant pathway.

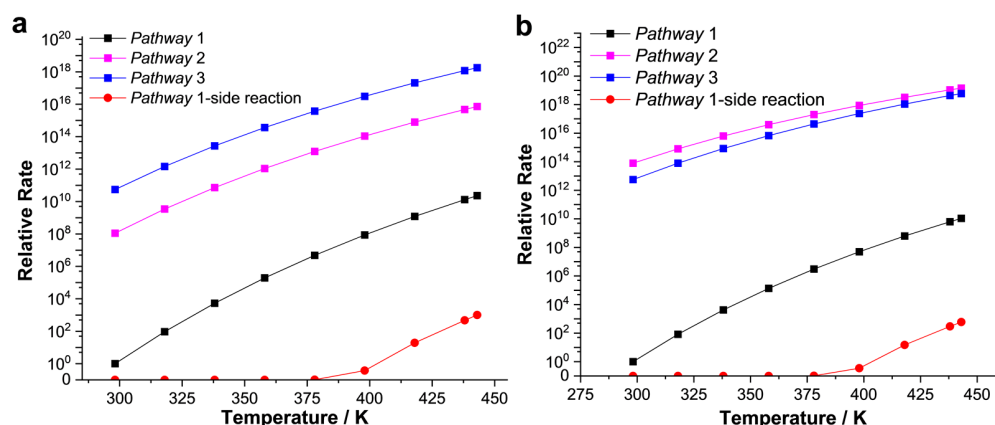


Figure 8. Chemical kinetics studies for catalytic system CAT-1 (a) and CAT-2 (b). Reaction rate constants versus the reaction temperature were carried out via TST calculation. The relative rate unit of CAT-1 and CAT-2 are $5.3 \times 10^{-30} \text{ s}^{-1}$ and $2.3 \times 10^{-29} \text{ s}^{-1}$, respectively.

3. Conclusions

Above all, we have theoretically studied the PNP pincer ligand-supported Ru^{II} platform used for catalyzing acetylene hydrochlorination. Unlike the traditional nucleophilic chloro-metalation of C_2H_2 , our study shows that the hydrochlorination of C_2H_2 is achieved via the electrophilic proton-metalation or synergistic addition when the metal center of the catalyst is electron-rich. As a late transition metal, ruthenium in +2 oxidation state has abundant 4d electrons to backdonate to the π -acidity ligand such as unsaturated hydrocarbon C_2H_2 . When using strong σ -donors as ligands, the adsorbed C_2H_2 can be nucleophilicity activated, thus favoring the electrophilic pathway for its hydrochlorination. Many studies have shown that the promotion of acetylene hydrochlorination catalysts requires electron-rich modification to enhance the adsorption and activation of HCl . Because this can increase the concentration of Cl^- in the system, which is conducive to the nucleophilic addition of adsorbed C_2H_2 [12,17,19–21,24]. In this work, we provide a new perspective to design ruthenium complex catalysts with higher potential activity, instead of changing the concentration to affect the chemical equilibrium but to establish different reaction mechanisms with more advantages in energy. Therefore, it is possible to study acetylene hydrochlorination under mild conditions or homogeneously from our perspective, which can effectively avoid sintering and carbon deposition in industrial non-mercury heterogeneous catalysts.

4. Materials and Methods

General Methods: Geometry optimizations, frequency calculations, and thermal corrections to the free energy (from 298 to 443 K) were performed at B3LYP-D3(BJ) level for all the intermediates and transition states. The exchange-correlation functional is B3LYP for all calculations. D3(BJ) stands for the dispersion correction of Grimme's dispersion method with Becke–Johnson damping. Def2-SVP basis set was assigned to short-period elements and MDF10 was used for ruthenium center [40–45]. Counterpoise corrections were considered for basis-set superposition errors (BSSE) in adsorption Gibbs free energy (ΔG_{ads}) calculations [46]. Since the fragmentation method is not unique, BSSE correction is only used on ΔG_{ads} . All calculations were performed using the Gaussian 09 package [47]. The computed structures were illustrated using CYL View [48].

To visualize the secondary interactions between catalyst and reactants, the independent gradient model (IGM) raised by Hénon group was used based on the optimized structures [49]. This method was implemented by Multiwfn, and the figure was presented by VMD [50,51].

The interaction between different species can be analyzed by means of an energy decomposition analysis (EDA) together with the natural orbitals for chemical valence (NOCV) method [52,53]. For this analysis, the intrinsic interaction energy (ΔE_{int}) between two fragments can be divided into for energy components (Equation (1)).

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} + \Delta E_{\text{disp}} \quad (1)$$

where the ΔE_{elstat} , ΔE_{Pauli} , ΔE_{orb} and ΔE_{disp} represent the electrostatic interaction, the Pauli repulsion, the orbital mixing/charge transfer, and the dispersion effect between two fragments, respectively. Importantly, the orbital term ΔE_{orb} can be further decomposed into contributions from each irreducible representation of the point group of the interacting system (Equation (2)).

$$\Delta E_{\text{orb}} = \sum_r \Delta E_r \quad (2)$$

The combination of the EDA with NOCV enables the partition of the total orbital interactions into pairwise contributions of the orbital interactions which is very vital to get a complete picture of the chemical interaction. The charge deformation $\Delta \rho_k(r)$, resulting from the mixing of the orbital pairs $\psi_k(r)$ and $\psi_{-k}(r)$ of the interacting fragments presents the amount and the shape of the charge flow due to the orbital interactions (Equation (3)), and the associated energy term ΔE_{orb} provides with the size of stabilizing orbital energy originated from such interaction (Equation (4)).

$$\Delta \rho_{\text{orb}}(r) = \sum_k \Delta \rho_k(r) = \sum_{k=1}^{N/2} v_k \left[-\psi_{-k}^2(r) + \psi_k^2(r) \right] \quad (3)$$

$$\Delta E_{\text{orb}} = \sum_k \Delta E_k^{\text{orb}} = \sum_{k=1}^{N/2} v_k \left[-F_{-k,-k}^{\text{TS}} + F_{k,k}^{\text{TS}} \right] \quad (4)$$

The EDA-NOCV analysis was performed by ORCA 5.0.2 [54] under the same level as the general calculation, where the basis set was transformed by using the fch2mkl module in the MOKIT package [55].

The reaction rate constants (k) of all discussed reactions were calculated using transition state theory (TST) [56,57].

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (5)$$

where h , k_B and R are the Planck, Boltzmann, and ideal gas constants, respectively. T represents the reaction temperature. $\Delta G^\ddagger$ is the activation free energy. The relative rate constant was used in kinetics studies of this work.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13010031/s1>, Figure S1. The Gibbs free energy profile for molecular complex **CAT**—2 catalyzed acetylene hydro-chlorination mechanism *pathway*-1; Figure S2. The Gibbs free energy profile for molecular complex **CAT**—1 catalyzed acetylene hydrochlorination mechanism *pathway*-2; Figure S3. The Gibbs free energy profile for molecular complex **CAT**—2 catalyzed acetylene hydrochlorination mechanism *pathway*-3; The xyz coordinates for intermediates and transition states (unit: Angstrom).

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