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NMR spectroscopic and computational investigations of RuHCl(CO)(PPh₃)₃ catalyzed isomerization of 1,4-cyclohexadiene



James X. Mao^{a,*}, Robert T. Mathers^b, Krishnan Damodaran^{a,*}

^a Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA
^b Department of Chemistry, Pennsylvania State University, New Kensington, PA 15068, USA

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ABSTRACT

Ruthenium catalysts with bulky ligands are particularly effective for diene isomerization reactions. Thermodynamics and the mechanism of RuHCl(CO)(PPh₃)₃ catalyzed 1,4-cyclohexadiene isomerization was probed experimentally through NMR spectroscopy and modeled theoretically using DFT and for the first time using ONIOM methods. Thermodynamics data (ΔH , ΔS and ΔG) measured by NMR experiments agree with the literature reported values. For theoretically obtained ΔH values, it was found MP2 method underestimates the enthalpy changes, RHF method overestimates them and DFT method behaves best among the three. Theoretical modeling of the mechanism of the isomerization reaction provided significant insight into the role of steric and electronic effects of the catalyst. A two-step decomposition analysis was carried out to separate steric and electronic effects induced by phenyl ligands of catalyst. It was shown that the steric effect decreases activation barriers, while the electronic effect increases the activation barriers.

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1. Introduction

Cyclic dienes find widespread use in organic, inorganic, and polymer chemistry. A few of the many examples include Diels— Alder reactions in organic chemistry, ligands on transition metal complexes, and monomers for polymerization. In the case of transition metal complexes with diene ligands, 1,4-cyclohexadiene (1,4-CHD), 1,3-cyclohexadiene (1,3-CHD) and 1,5-cyclooctadiene (1,5-COD) are commonly encountered. For example, these dienes and others, such as 1,3-butadiene, will coordinate to nickel [28], iron [15], ruthenium [9], cobalt [24], and manganese [20] as well as many other transition metals. Additionally, Ni(1,5-COD)₂ is a commercially available precursor for many nickel complexes.

Recently, we reported a solvent-free method for synthesizing renewable 1,3-CHD from plant oils [26]. A key step in this method was the isomerization of 1,4-CHD to 1,3-CHD as an alternative to dehydrohalogenation reactions (Fig. 1). Alkene isomerization with transition metal complexes has been examined by many researchers using complexes based on ruthenium [21], rhodium [37], platinum [21], iron [31], nickel [41], titanium [29,33], and zirconium [29]. The well-known mechanism for many of these

isomerization catalysts initially involves coordination of an alkene to a metal center followed by insertion (oxidative addition) into a metal hydride bond. Subsequently, reductive elimination at a β carbon allows isomerization of an alkene to an adjacent position.

The catalyst RuHCl(CO)(PPh₃)₃ was found to be highly active for the isomerization of six-membered cyclic dienes. This ruthenium hydride catalyst was originally reported by Vaska and DiLuzio [44]. In the last five decades, numerous chemical transformations involving coupling reactions [12], hydrogenation [27], hydrosilylation [25], and isomerization [6,46] reactions have been reported with this complex. This same catalyst also isomerized acyclic dienes such as the two non-conjugated alkenes in linoleate esters [46]. After 24 h, the formation of conjugated alkenes with 0.5–1 mol% catalyst occurred with yields as high as 95% and turn over frequencies (TOF) of ~5 h⁻¹.

Given the propensity of cyclic dienes to coordinate to transition metal complexes and act as ligands, it was a little surprising to determine that Vaska's RuHCl(CO)(PPh₃)₃ catalyst would isomerize neat 1,4-CHD to 1,3-CHD with TOF values as high as 5000 h⁻¹. The observed TOF values were approximately a thousand times larger than the values reported for the acyclic dienes in methyl linoleate. Additionally, the yields for isomerizing acyclic dienes and CHD were very different due to the thermodynamic stability differences [17,43]. As a result, we were interested to investigate the mechanism. Rationalization of the influence of catalyst, especially the role of its

^{*} Corresponding authors. E-mail addresses: damodak@pitt.edu, damodak@gmail.com (K. Damodaran).

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bulky ligands, is crucial to develop more selective catalysts for this type of reactions in future. In this work, we report our theoretical investigations of the catalytic isomerization mechanism for 1,4-CHD.

2. Computational methods

Calculations were performed using the Gaussian 09 program [11]. Thermodynamics data were calculated using RHF (Restricted Hartree-Fock). DFT (Density Functional Theory) and MP2 (secondorder Møller–Plesset) methods using 26 different basis sets (listed in Supporting information). Calculations for the mechanism were carried out at Density Functional Theory (DFT) level with the hybrid functional B3LYP, which incorporates Becke's three-parameter exchange functional [5] and the Lee, Yang, and Parr correlation functional [22]. Stuttgart RECPs and associated basis sets [3] were used for Ru and P atoms, and 6-311G(d) basis sets [10] for all other atoms. UFF method [34] was employed for the molecular mechanics calculations within the ONIOM methodology [38]. The nature of all energy minima and transition states was confirmed via analytical frequency calculations. Transition states were further characterized by mimicking the unique imaginary frequency to confirm their relaxations to correct corresponding local minima. Quantum theory of atoms in molecules (QTAIM) analysis was carried out by AIMALL software [18].

3. Chemicals and experiments

All the samples were purchased from Acros Organics and were used without further purification. The catalyst, RuHCl(CO)(PPh₃)₃ was loaded into the NMR tube under nitrogen atmosphere and dissolved in deuterated benzene, followed by the addition of 1,4-CHD.

All the NMR experiments were performed on a Bruker Avance III 600 MHz spectrometer equipped with a 5 mm BBFO Plus probe and the accuracy of the temperature controller was +0.1 K. The reaction mixture was allowed to equilibrate for about 12 h before the NMR measurements. The temperatures were calibrated using 80% ethylene glycol in DMSO- d_6 .

4. Thermodynamics

The mole fraction of 1,3-CHD was obtained from the ratio of the integrals of the 1,3-CHD and 1,4-CHD resonances in the ¹H NMR spectra of the reaction mixture in benzene- d_6 . Equilibrium constants were calculated from mole fraction, with the effect of statistical factor considered (1,3-CHD is statistically favored over 1,4-CHD by a factor of 2). Equilibrium constants (*K*) and free energy changes ($\Delta G = -RT$ In *K*) as a function of temperature (*T*) are reported in Table 1. The enthalpy change (ΔH) and entropy change

Table 1

Measured equilibrium constants for RuHCl(CO)(PPh_3)_3 catalyzed isomerization of 1,4-CHD as a function of temperature.

<i>T</i> (K)	K	ΔG (kJ/mol)		
303	0.9564	0.11		
314	0.9682	0.08		
324	1.0110	-0.03		
335	1.0423	-0.12		
345	1.0820	-0.23		



Fig. 2. Free energy change as a function of temperature for $RuHCl(CO)(PPh_3)_3$ catalyzed 1,4-CHD isomerization reaction.

 Table 2

 Thermodynamics data of 1,4-CHD isomerization.

	In solution		Gas phase		
	Literature (in Me ₂ SO) [40]	NMR (in C ₆ D ₆)	Literature	B3LYP/ 6-311++G	MP2/cc-pVTZ
$\Delta H/kJ \text{ mol}^{-1}$ $\Delta S/J \text{ mol}^{-1}$	1.6 4.4	2.7 8.4	-2.1 [39] -5.9 [30]	-1.79 -4.54	-3.98 -5.25
$\Delta G/kJ \text{ mol}^{-1a}$	0.24	0.26			

^a At 298K.



Fig. 3. HOMO and LUMO energy diagram of 1,3-CHD, 1,4-CHD, and RuHCl(CO)(PPh₃)₂. Red regions in orbitals indicate the positive phase while green present the negative phase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)





Fig. 4. Computed reaction profile of catalytic 1,4-CHD isomerization at B3LYP/6-311G(d) level. Enthalpies (kJ/mol) are quoted relative to 6. Phenyl substituents on the phosphine ligands are replaced by hydrogen atom for simplicity.

 (ΔS) were obtained from the plot of free energy change vs. temperature (Fig. 2). The results are listed in Table 2 and compare with previous reported data.

The enthalpy change (ΔH) between conjugated 1,3-CHD and unconjugated 1,4-CHD was surprisingly small [4,35]. It was reported as -1.1 kJ/mol in acetic acid [43], -2.1 kJ/mol in liquid state [35], and 1.6 kJ/mol in Me₂SO [40]. Our measurements from NMR spectroscopy gave 2.67 kJ/mol in C₆D₆.

The enthalpy change (ΔH) of the isomerization reaction was also calculated using computational methods. A benchmark study was done to determine the quality of basis sets at different computational methods in predicting the experimental enthalpy data. Twenty-six different basis sets at three different methods, RHF (Restricted Hartree–Fock), DFT (Density Functional Theory) and MP2 (Second-order Møller–Plesset) were used (Data in Supporting information Table S5). The difference between calculated and reported experimental [39] enthalpy changes in gas state is compared (Fig. S1 in Supporting information). MP2 method underestimates the enthalpy changes and RHF method overestimates them. DFT (B3LYP) method seems to be the best among the three in reproducing the experimental values. We also calculated the enthalpy change in C₆H₆ solution using polarizable continuum method (PCM) [42]. The results are very similar to the gas phase calculations.



Fig. 5. Bond critical points (red) in reaction regions of TS-1 and TS-2. Only atoms of interest are shown for simplicity. Ruthenium (green) and hydrogen (white) atoms are from catalyst molecule, and carbon (gray) atoms are from cyclohexadiene molecule. (a) TS-1 (b) TS-2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The entropy change (ΔS) was reported as 4.4 J/mol in Me₂SO [40] and -5.9 J/mol in gas phase [30]. Calculations show MP2 method produces better results than DFT method (Table 2). In gas state, the entropy change is negative due to high conformational flexibility of 1,4-CHD [36]. It changes to positive in liquid/solution state, likely due to high structural symmetry of 1,4-CHD and a resulting ordered solute–solute or solute–solvent interactions from this structural symmetry.

5. Mechanism of the isomerization reaction

In the first step of the catalytic isomerization reaction, a triphenyl phosphine ligand dissociates from RuHCl(CO)(PPh₃)₃ to form RuHCl(CO)(PPh₃)₂. Subsequently, an available orbital on ruthenium is able to coordinate to the π bonds on 1,3-CHD or 1,4-CHD. Frontier orbitals involved in the catalytic process were calculated to confirm the process (Fig. 3). The diagram clearly shows that the reaction involves π electron pairs of CHD and the empty orbital on the Ru atom of the catalyst. 1,3-CHD or 1,4-CHD first coordinates to the Ru atom, followed by the process of isomerization.

The computed lowest-energy reaction profile of the catalytic 1,4-CHD isomerization is shown in Fig. 4. After 1,4-CHD attaches to catalyst and forms complex **1**, the hydrogen atom from the catalyst is added to 1,4-CHD to form metal complex **3**. The step from **1** to **3** is a reverse β -hydride elimination, and the step from **4** to **6** is a forward β -hydride elimination. In a β -hydride elimination, an alkyl group bonded to a metal center is converted into a corresponding metal-bonded hydride and an alkene.

The rate determining step of the catalytic isomerization is the formation of transition state (Fig. 4). The two transition states of forward and reverse β -hydride eliminations (TS-1 and TS-2), as well

Table 3Electron densities at BCPs in TS-1 and TS-2.

	BCPs in TS-1			BCPs in TS-2				
	Ru–H	C–C	Ru–C	С—Н	Ru-H	C–C	Ru–C	C-H
ρ/e	0.114	0.289	0.082	0.090	0.111	0.287	0.086	0.095



Fig. 6. Energy diagram (in unit kJ/mol) of catalytic 1,4-CHD isomerization to show steric effect. The blue diagram is from B3LYP calculations with PH₃ ligands; the cyan diagram is from ONIOM(B3LYP:UFF) calculations with PPh₃ ligands. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

as the energy barriers associated with them, undoubtedly play critical roles in the isomerization process. They were confirmed as the correct transition states first by intrinsic reaction coordinate calculations carried out by Gaussian 09. The forward and reverse paths lead to correct reactants and products. They were further analyzed by Bader's quantum theory of atoms in molecules (QTAIM) method [19,32]. In QTAIM analysis, the presence of a bond critical point (BCP) in the electron density field between atoms is indicative of a bonding between them. Electron densities ρ at critical points are used to characterize the bonding feature. A strong bonding is accompanied by high densities. The results of QTAIM analysis are shown in Fig. 5 and Table 3. The BCPs between Ru–H and C–H (Fig. 5), as well as the electron densities at these BCPs (Table 3), clearly indicate that the hydrogen atom is bonded both to ruthenium catalyst and CHD in these transition state structures.

The bulky phenyl groups of the catalyst could strongly influence the reactivity of transition states by preventing the coordination positions or by altering electronic structure of ruthenium center. To distinguish steric and electronic factors of the phenyl groups, ONIOM methodology [38] was employed to analyze the energy diagram change of the catalytic isomerization reaction. ONIOM methods have been widely used to study reaction mechanisms involving transition metal complexes [7,8,13,14,16,23,45,47], but as far as we know this is the first ONIOM investigation of the alkene isomerization process.

In a two-layer ONIOM method, the full molecular system under investigation is referred to as real system. A small but most important part of the real system, which is normally the part where the bond formation and breakage occur, is referred as model system. The real system is treated at relatively low computational levels, and the model system is treated at more accurate computational levels. The energy is calculated as:

 $E^{\text{ONIOM}} = E^{\text{real,low}} + E^{\text{model,high}} - E^{\text{model,low}}$

For our ONIOM investigations of 1,4-CHD isomerization by RuHCl(CO)(PPh₃)₃, all atoms except those from phenyl groups are treated as model system. The real system is treated at molecular mechanics (MM) level by UFF method [34], and the model system is

treated at quantum mechanics (QM) level by density functional theory (DFT).

A two-step decomposition analysis [1,2] was carried out to decompose steric and electronic effects induced by PPh₃ ligands. To accomplish this, three different calculations were performed:

- 1. QM-PPh₃: full Quantum Mechanics (QM) calculation of the whole system. In a full QM calculation, both steric and electronic effects from PPh₃ ligands are included.
- 2. QM-PH₃: full Quantum Mechanics calculation of the whole system, but the PPh₃ ligands were modeled as PH₃ ligands. In this simplified model, neither steric nor electronic effects from PPh₃ ligands are included since all the Ph₃ groups are replaced by H atom.
- 3. ONIOM(QM:MM): the whole molecular system is treated with QM except PPh₃ ligands which are treated with Molecular Mechanics (MM). In this ONIOM calculations, only steric effects from PPh₃ ligands are included. Electronic effects are not included since PPh₃ ligands are not treated in QM level.

All the calculations were carried out using optimized geometries resulting from the DFT calculations. As a first step of the decomposition analysis, evaluation of steric effects was performed by comparing, QM-PH₃ versus ONIOM(QM:MM). As a second step, electronic effects were analyzed by comparing QM-PPh₃ versus ONIOM(QM:MM). The results are shown in Figs. 6 and 7.

It was found both the steric and electronic effects influence the transition states as well as the initial and final metal complexes, and they changed the reactivity in opposite manner: the steric effect introduced by PPh₃ ligands decreases activation barriers of rate determining step (from 26 kJ/mol to 17 kJ/mol, Fig. 6), while the electronic effect increased the activation barriers (from 17 kJ/mol to 23 kJ/mol, Fig. 7). The steric repulsions should destabilize all complexes, including transition states, initial and final complexes. The decrease of activation barrier suggests that initial and final complexes are more destabilized than transition states. However, electronic effects from PPh₃ ligands increase the barrier about 6 kJ/mol. These calculations provide insight for developing new catalysts in future: different bulky ligands, which may provide same



Fig. 7. Energy diagram (in unit kJ/mol) of catalytic 1,4-CHD isomerization to show electronic effect. The red diagram is from B3LYP calculations with PPh₃ ligands; the cyan diagram is from ONIOM(B3LYP:UFF) calculations with PPh₃ ligands. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

important steric effects to lower the energy barrier but different electronic effects not to increase the barrier, might work better to catalyze the isomerization process.

6. Conclusion

In summary, catalytic 1,4-CHD isomerization reaction was investigated experimentally and theoretically. Thermodynamic data were obtained from NMR spectroscopy as well as ab initio calculations. DFT, QTAIM and ONIOM methods have been employed to probe the mechanism of catalytic 1,4-CHD isomerization. Calculations show the different roles of steric and electronic effects induced by phenyl ligands from catalyst RuHCl(CO)(PPh₃)₃: the steric effect decreases activation barriers while the electronic effect increases the activation barriers. We believe these results will provide a starting point for further experimental development of more efficient catalysts.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.05.015.

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