

REGULAR ARTICLE

Mechanism of CO₂ Activation by (PNN)Ru(H)(CO) Complex

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Abstract: The reaction mechanism for CO₂ activation by (PNN)Ru(H)(CO) was comprehensively investigated by means of density functional theory method. The theoretical results indicate that: 1) isomer **1** (with methylene in phosphorus side arm) is more stable than **2** (with methylene in amide side arm) by 6.45 kcal/mol, and two hydrogen migration steps with barrier heights of 49.95 and 38.24 kcal/mol, respectively, are involved in the tautomerism between **1** and **2**; 2) The direct [1,3]-addition of CO₂ to **1** and **2** affords **4** and **5**, respectively, by forming new C-C and Ru-O bonds. The addition barriers are calculated to be 9.83 and 6.66 kcal/mol, while the decomposition barriers of **4** and **5** are 7.97 and 19.38 kcal/mol, respectively; 3) Reverse [1,3]-additions leading to **6** and **7** are thermodynamically and kinetically unfavorable. The frontier molecular orbital analysis shows that CO₂ [1,3]-addition leading to **4** and **5** is preferred to inverse [1,3]-addition leading to **6** and **7**, respectively.

AMS subject classifications: 65D17, 65D18, 68U05, 68U07

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1. Introduction

In the past few decades, cooperative catalysis based on new modes of metal ligand

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cooperation has experienced an explosive progress for their powerful catalytic activity in the asymmetric synthesis. PNN-, PNS- and PNP-type ruthenium pincer complexes have shown substantial catalytic activity in a variety of reactions [1-5]. A series of recent reports by Milstein have demonstrated that pincer-ligated Ru complexes such as (PNN)Ru(H)(CO) (PNN=6-(di-tert-butylphosphinomethylene)-2-(N,N-diethylaminomethyl)-1,6-dihydropyridine) and (PNP)Ru(H)(CO) (PNP=2,6-(di-tert-butylphosphinomethylene)-1,6-dihydropyridine) are highly effective catalysts for the hydrogenation of carbonyl compounds, including esters, amides, and carbamides[6-16].

2012, Milstein and co-workers [17] reported the cooperative [1,3]-addition of CO₂ to the unsaturated PNP-pincer complex [Ru(PNPtBu*)(H)(CO)]. Their experimental results showed that CO₂ [1,3]-addition via forming new C-C and Ru-O bonds was proved to be the most feasible reaction mode, and they demonstrated that dispersion correction is very important in mechanism study by density functional theory.

2012, Sanford and co-workers reported the activation of CO₂ at (PNN)Ru(H)(CO) via C-C coupling with the pincer ligand in conjunction with Ru-O bond formation under mild condition [18]. The discoveries have great practical significance in synthetic chemistry as well as the reutilization of carbon dioxide [19]. Although Sanford and co-workers proposed similar catalytic mechanism as CO₂ activation by PNP-Ru complex [17], the detailed mechanism, especially the information of the rate-determining step of CO₂ activation by PNN-Ru complex, is still unknown.

In this paper, we present the computational investigations into the mechanism of the CO₂ activation reaction by (PNN)Ru(H)(CO) using the density functional theory. The mechanisms of tautomerization between the two isomers of (PNN)Ru(H)(CO), and their [1,3]-addition reaction with CO₂ were fully considered. The essential role of noninnocent pincer ligand in the rate-determining step of CO₂ activation processes was revealed and analyzed in depth.

2. Computational Methods

All geometric optimizations and vibration analysis were performed with the Gaussian03 program package [20]. B3LYP method with combined basis set, 6-311G (d, p) for all nonmetal atoms and Def2-SVP for Ru atom, was employed in all the calculations. Geometries of all the stationary points, including reactants, products, intermediates and transition states, were fully optimized without any constrains. All the minima and transition states were further proved by vibrational analysis to ensure no imaginary mode for minima, and one and only one imagine mode for transition states. Intrinsic reaction coordinate (IRC)