Journal of Organometallic Chemistry 811 (2016) 29–39

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Electron-donating groups and high ring strain promoted ring opening of methylenecyclopropanes catalyzed by rhodium and iridium complexes

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ARTICLE INFO

Article history:
Received 2 December 2015
Received in revised form
23 February 2016
Accepted 8 March 2016
Available online 10 March 2016

Keywords:
Ring-opening
DFT
Methylenecyclopropanes
Electron-donating groups

ABSTRACT

The possible ring-opening pathways of X-substituted MCPs (X = NO_2, CF_3, F, H, Ph, CH_3, OH, NH_2) promoted by $MH(CO)(PY_3)_3$ (M = Rh, Ir, Y = H, Ph) and Wilkinson's catalyst-$[RhCl(PY_3)_3]$ (Y = H, Ph) were studied by density functional theory. The ring-opening reaction was initiated by the orbital interaction between the transition metal of catalyst and reactant MCP. The strong coordination ability of Ir with C=C double bond and the inertness of complex intermediate caused the difficulty in further reaction steps of catalyst dissociation and hydride transfer, rationalizing that $IrH(CO)(PPh_3)_3$ catalyzed ring-opening reaction occurred at higher temperature (50 °C) than the $RhH(CO)(PPh_3)_3$ catalyzed one (room temperature). Without the medium hydride in $RhCl(PPh_3)_3$ catalyst, the C=C bond of MCP cannot insert into the Rh–H bond and the hydride cannot be borrowed from $RhCl(PPh_3)_3$ like $RhH(CO)(PPh_3)_3$ catalyst, hence making the $RhCl(PPh_3)_3$-catalyzed reaction much more difficult to occur. The ring-opening step is predicted to be the rate-determining step for $MH(CO)(PPh_3)_3$ catalyst, which is different from the Cp_2LnH (Ln = La, Lu) catalyzed reactions. Multifaceted factors of substituents including ring strain, electron-donating ability, and the steric effect of the substituents were revealed for $MH(CO)(PPh_3)_3$ catalyzed reactions when M = Rh and Ir. The hydroxyl substituted MCP (X = OH) bears not only higher ring strain but also the stronger electron-donating ability, leading to the lowest activation energy among the studied systems. Understanding of the multifaceted factors of substituents is useful for regulating the ring-opening reaction of substituted MCP promoted by transition metal complexes.

1. Introduction

Methylenecyclopropanes (MCPs), which are characterized with a three-membered ring and an *exo*-methylene moiety, have been served as useful building blocks in organic synthesis [1]. The ring-opening reactions of substituted MCP reactants (called R in this work) catalyzed by transition metal complexes (such as Rh, Ir, Pd, Pt and La) have attracted significant interest [2,3]. The ring-opening reactions can take place through cleavage of the proximal bonds (C2–C3 or C2–C4 bond) or distal C3–C4 bond (shown in Scheme 1). Especially, the cleavage of proximal bond of MCPs can produce butadienes, which are important industrial chemicals.

Osakada et al. reported a series of ring opening reactions cleaving proximal bond (C2–C3 or C2–C4 bond) of phenyl substituted MCPs (X = Ph) catalyzed by Rh and Ir complexes, $MH(CO)(PPh_3)_3$ (M = Rh, Ir) [3]. In the presence of the catalyst $RhH(CO)(PPh_3)_3$, ring-opening reaction of Ph-substituted MCPs proceeds at room temperature within 10 min via selectively cleaving the sterically less hindered C2–C3 bond to give 2-phenyl butadiene [3d]. However, the catalyst $IrH(CO)(PPh_3)_3$ seems to be less aggressive to react with Ph-substituted MCP and the ring-opening reactions occurs at room temperature within 24 h to obtain an intermediate Ir complex [3d]. Only when the temperature is increased to 50 °C, the three-membered ring is broken by $IrH(CO)(PPh_3)_3$ catalyst within 40 h to yield the main product, 2-phenyl butadiene [3a]. Different from $MH(CO)(PPh_3)_3$ catalysts with

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http://dx.doi.org/10.1016/j.jorganchem.2016.03.006
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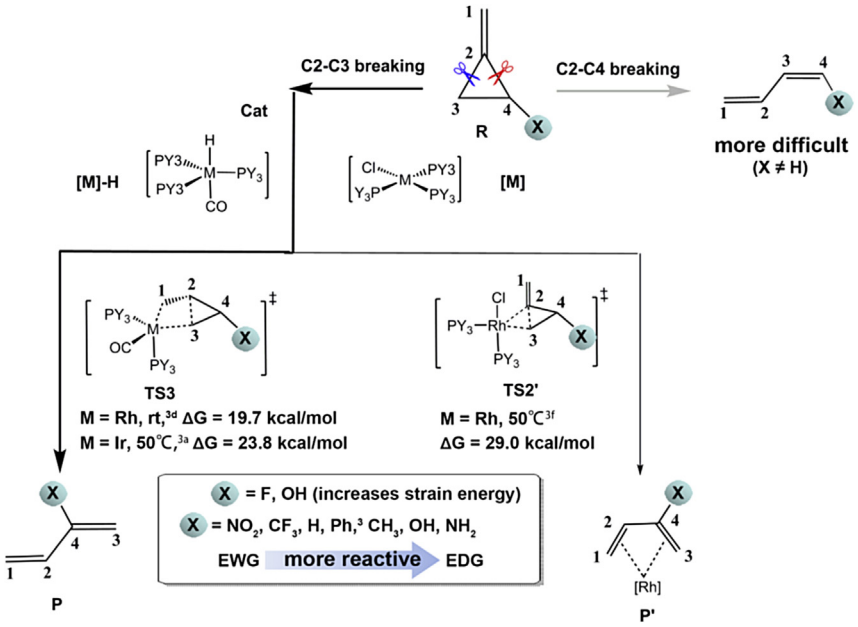

Scheme 1. $MH(CO)(PY_3)_3$ vs. $RhCl(PY_3)_3$ (Y = Ph) catalyzed the ring opening of substituted MCP.

hydrogen ligand, Wilkinson's catalyst-[$RhCl(PPh_3)_3$] without hydrogen ligand needs extra energy to facilitate the ring-opening reaction of Ph-substituted MCPs (X = Ph), which takes place at 50 °C [3f]. This work is motivated by these interesting experimental phenomena: Why for the similar trigonal-bipyramidal $MH(CO)(PPh_3)_3$ catalysts, ring opening reactions catalyzed by $IrH(CO)(PPh_3)_3$ is more difficult than that catalyzed by $RhH(CO)(PPh_3)_3$? Containing the same transition metal center, Rh, why the ring opening catalyzed by H–free $RhCl(PPh_3)_3$ catalyst proceeds at higher temperature than that catalyzed by $RhH(CO)(PPh_3)_3$ with hydrogen ligand?

Osakada et al. proposed the ring-opening mechanisms of MCPs catalyzed by [M]–H (M = Rh, Ir) catalyst according to the experiments [3a,3b,3c]. They speculated that the ring opening proceeds via the initial insertion of a C=C double bond of MCPs into the M–H bond followed by the C–C bond cleavage of the three-membered ring and finally gave the diene product through β-H elimination. Miyamoto et al. computationally studied the ring opening mechanism of MCPs catalyzed by lanthanide complex, Cp_2LnH (Ln = La, Lu, also called [Ln]-H) using quantum chemical molecular dynamics simulation and density functional theory (DFT) [4]. Computational results indicated that the ring opening undergoes the initial insertion of the C=C double bond of MCPs into the Ln–H bond with a subsequent hydrogen transfer followed by the ring opening of the proximal bond. The [La]-H catalyst contains metallocene ring ligands and the final product of the catalyzed reaction is a mono-olefin lanthanide complex, different from that obtained in the $RhH(CO)(PPh_3)_3$ or $IrH(CO)(PPh_3)_3$ catalyzed reactions. It is not clear whether the computational ring-opening paths catalyzed by [La]-H with hydrogen ligand are the same as those catalyzed by other transition metal catalysts with hydrogen ligand? In addition, Wilkinson's catalyst, $RhCl(PPh_3)_3$, without hydrogen ligand, should go through different reaction paths to catalyze the ring-opening reaction from those $RhH(CO)(PPh_3)_3$ catalyzed reaction. For example, $RhCl(PPh_3)_3$-catalyst cannot initiate the insertion of C=C double bond of MCPs into the Rh–H bond. The reason behind the different behaviors of different catalysts is intriguing and poorly understood.

Besides the influence of different catalysts on the ring-opening reaction, the effect of substituents on MCPs has attracted the interest of both experimental and theoretical chemists. The experiments of ring-opening rearrangement of 1,1-difluoro-2-MCPs indicated that the rate of rearrangement reaction was enhanced substantially by the presence of the fluorine substituents [5]. DFT calculation results further indicate that the germinal fluorines substituted MCPs can improve the ring strain and destabilized the three-membered ring thermodynamically, hence reducing the activation energy of the rearrangement [6]. It is also expected that the ring-opening reaction rate can be regulated by changing the substituents on MCP ring from an electron-withdrawing group (EWG) to an electron-donating group (EDG). For the same three-membered cyclopropane (without the olefinic moiety in MCP), Kirihara et al. experimentally studied the substituents effects on the substituted cyclopropanes and found that an electron-donating group (EDG) at C2 of the tertiary cyclopropanol silyl ethers promoted ring opening in the reaction with diethylaminosulfur trifluoride [7]. Motivated by the above theoretical and experimental results, we attempt to introduce different substituents into MCP ring to regulate the reactivity of ring-opening reactions.

In this work, we will study the ring-opening pathways of MCPs catalyzed by $MH(CO)(PY_3)_3$ and $RhCl(PY_3)_3$ (M = Rh, Ir and Y = H, Ph) in order to investigate the role of the catalysts and to explore the effect of substituents (X = NO_2, CF_3, F, H, Ph, CH_3, OH, NH_2) at a ring carbon on ring opening reactivity. Multifaceted factors of substituents including ring strain, electron-donating ability, and the steric effect of the substituents will be revealed. It will be shown that fluorine substituted MCP (X = F) with the highest ring strain lowers the activation energy and promotes the $RhH(CO)(PPh_3)_3$-catalyzed ring-opening reaction. The hydroxyl substituted MCP (X = OH) bears not only higher ring strain but also the stronger electron-donating ability, leading to the lowest activation energy among the studied systems. These insights are useful for understanding and controlling the ring opening reaction of substituted MCP promoted by transition metal complexes.

2. Computational details

All the DFT calculations were performed with Gaussian 09