Chinese Chemical Letters 26 (2015) 58–62

Contents lists available at ScienceDirect

Chinese Chemical Letters

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

Original article

Mechanistic study on the regioselectivity of Co-catalyzed hydroacylation of 1,3-dienes

Yuan-Ye Jiang [a,b], Hai-Zhu Yu [b,*], Jing Shi [a,*]

[a] Department of Chemistry, University of Science and Technology of China, Hefei 230026, China
[b] Department of Polymer Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China

ARTICLE INFO

Article history:
Received 8 July 2014
Received in revised form 11 September 2014
Accepted 29 September 2014
Available online 1 November 2014

Keywords:
Density functional theory
Cobalt
Regioselectivity
Hydroacylation

ABSTRACT

Density functional theory (DFT) method was used to explore the origin of the regioselectivity of Co-catalyzed hydroacylation of 1,3-dienes. The reaction of 2-methyl-1,3-butadiene and benzaldehyde with 1,3-bis(diphenylphosphino)propane ligand was chosen as the model reaction. The energies of the intermediates and transition states in the stages of oxidative cyclization, β-H elimination and C-H reductive elimination were investigated. Computational results show that β-H elimination is the rate-determining step for the whole catalytic cycle. C1-Selective oxidative cyclization is favored over C4-selective oxidative cyclization. Besides, C4-selective oxidative cyclization is kinetically disfavored than all the steps in C1-hydroacylation mechanisms, consistent with the experimentally obtained C1-selective hydroacylation products. Analyzing the reason for such observation, we suggest that both electronic and steric effects contribute to the C1-selectivity. On the electronic aspect, C1 is more electron rich than C4 due to the methyl group on C2, which makes the electrophilic attack of aldehyde carbon on C1 more favorable. On the steric aspect, the methyl group locates farther from the ligands in the transition state of C1-selective oxidative cyclization than in that of C4-selective oxidative cyclization.

1. Introduction

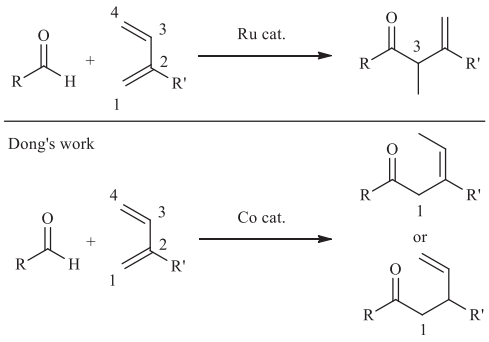
First-row transition metals are more abundant and less expensive than precious transition metals like Pd, Rh and Ru, and this character promotes the rapid development of various first-row metals catalyzed cross-coupling reactions [1]. In this context, Co-catalyzed organic transformations such as cycloaddition reactions, reduction reactions, Aldol reactions, Michael reactions, hydrovinylation reactions, hydroacylation reactions have achieved many attractive results [2]. Another amazing reason for the exploitation of first-row transition metals is that a different chemical- or regioselectivity could be realized by replacing the precious transition metal catalyst with the first-row transition metal catalyst. For example, in the Ru-catalyzed hydroacylation of 2-substituted 1,3-diene reported by Krische [3] and Ryu [4], C–C bond selectively forms at the C3 site (Scheme 1). However, Dong *et al.* recently reported Co-catalyzed hydroacylation of 2-substituted 1,3-diene, in which C–C bond selectively forms at the C1 site [5].

As to the mechanism of Co-catalyzed hydroacylation of 1,3-diene, Dong *et al.* proposed the oxidative cyclization pathway (Path A, Scheme 2). In this mechanism, the pre-catalyst Co^{II} complex is first reduced by $In/InBr_3$ to the active Co^{I} complex **A** [5–7]. Then C1-selective oxidative cyclization occurs on Co^{I} complex to give the Co^{III} complex **B**. β-H elimination occurs on **B** give the hydride complex **C**. Finally, C–H reductive elimination on **C** gives the product and regenerate the catalyst A. Similar to Path A, the oxidative cyclization of 1,3-diene and aldehyde also possibly occurs at the C4 site, which will finally produce a C4-selective product (Path B, Scheme 2). Interestingly, only trace amount of C4-selective products were obtained in Dong's reactions.

Our recent research interests cover the Co-catalyzed cross-couplings, such as the investigations on origin for ligand controlled regioselectivity in Co-catalyzed hydroarylation of styrene [8]. In the present study, we systematically investigated the mechanism of Co-catalyzed hydroacylation of 1,3-diene with DFT method. The calculation results indicate that β-H elimination is the rate-determining step in the proposed catalytic cycle. C4-selective oxidative cyclization is kinetically disfavored than the pathway of C1-selective oxidative cyclization and its following steps. Further analysis shows that both the electronic and steric effects of the

* Corresponding authors.
E-mail addresses: yuhz@ustb.edu.cn (H.-Z. Yu), shijing@ustc.edu.cn (J. Shi).

http://dx.doi.org/10.1016/j.cclet.2014.10.021



Scheme 1. Different regioselectivity of hydroacylation of 1,3-diene by different transition-metal catalysts.

2-substituted group of 1,3-diene contribute to the dominance of C1-selective oxidative cyclization.

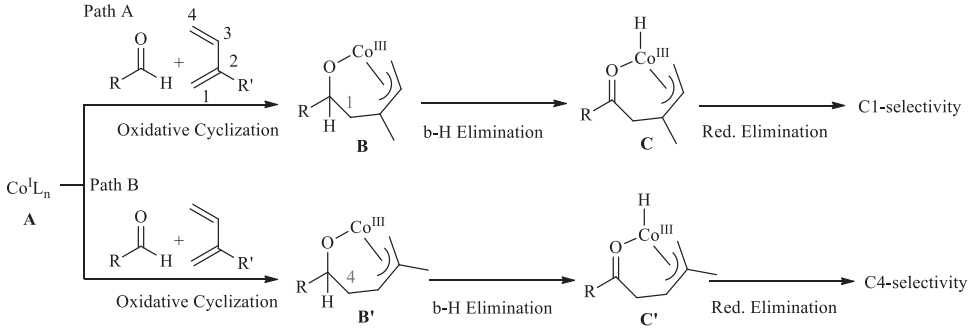
2. Computational details

Co-catalyzed cross coupling of benzaldehyde **1a** and 2-methyl-1,3-butene **2a** with the dppp ligand (dppp = 1,3-bis(diphenylphosphino)propane) was chosen as the model reaction for mechanistic studies (Scheme 3). Computational studies were performed with Gaussian 09 program [9–23]. Geometry optimization was conducted in gas phase with M06 method [24]. The effective core potential of LANL2DZ with the associated valence basis set [25] was used describe Co and I atoms while 6-31G(d) basis set was used for the other atoms. At the same level of theory, frequency analysis was performed to confirm that the optimized structure was either a minimum or a transition state, and also to obtain the thermodynamic energy correction. To reduce the overestimated entropy effect due to the gas-phase optimizations, Sakaki's strategy by omitting the electronic and rotational entropic contributions is used [26,27]. In addition, solution-phase single point energies were calculated with a larger basis set based on the optimized structure, *i.e.* SDD [28] for Co and I while 6-311+G(d,p) for the rest atoms. SMD model was used for solution-phase single point energy calculations (solvent = dichloroethane) [29]. The reported energies were the solution-phase single point energies corrected by gas-phase Gibbs free energy corrections, corresponding to 1 mol/L and 298 K.

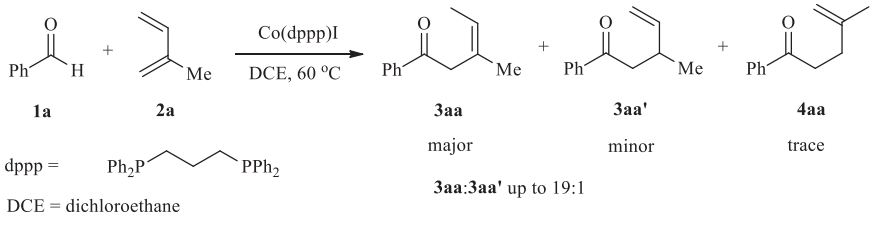
3. Results and discussion

The energy profile of Path A was investigated first and the results were shown in Fig. 1. The ligand exchange of the neutral Co^{I} complex **1** with aldehyde **1a** and diene **2a** gives the cationic Co^{I} complex **2**, which causes an energy decrease of 22.8 kcal/mol. In complex **2**, Co is coordinated by the C3 and C4 double bond (Fig. 1). Then the oxidative cyclization occurs *via* the transition state **TS1** and generates the intermediate **3**. This step further causes an energy decrease of 8.5 kcal/mol, and its energy barrier is only 4.5 kcal/mol. With the formation of the new C–C bond, the lengths of several other C–C bonds of **2a** are changed during the transformation from **2** to **3**. The C1–C2 bond is lengthened from 1.342 Å to 1.491 Å, C2–C3 bond is shortened from 1.472 Å to 1.386 Å, C3–C4 bond is lengthened from 1.389 Å to 1.428 Å. Meanwhile, the C–O bond of **1a** changed from 1.235 Å to 1.393 Å. Besides, the coordination mode of **2a** changes from η^2 (in **2**) to η^3 (in **3**).

The intermediate **3** then undergoes β-H elimination *via* the four-membered transition state **TS2** to generate the complex **4a**. In this step, a remarkable distortion of the cyclometallic ring occurs to make the hydrogen atom on the phenyl-substituted carbon get close to the Co center. As a result, a high energy barrier for β-H elimination (20.8 kcal/mol from **3** to **TS2**) is required. Along with the transformation from **3** to **4a**, the C–O bond of **1a** shortens to 1.241 Å, which is close to the C=O bond length of **1a** in complex **2**. In **4a**, Co is coordinated by a carbonyl group and an allyl anion. The carbonyl locates *cis* to the hydride and the allyl anion locates *trans* to the hydride.



Scheme 2. Proposed mechanism for C1-selectivity in Co-catalyzed hydroacylation of 1,3-diene and its competitive mechanism for C4-selectivity.



Scheme 3. Model reaction for mechanistic study.