



Orbital phase in organolanthanide-catalyzed reactions: hydroamination/cyclization



Satoshi Inagaki^{a,b,*}, Hirotaka Ikeda^c

^a Institute of Science and Technology Research, Chubu University, 1200 Matsumoto, Kasugai, Aichi 487-8501, Japan

^b Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

^c Computational Science Department, Science and Technology Systems Division, Ryoka Systems Inc., Tokyo Skytree East Tower, 1-1-2, Oshiage, Sumida-ku, Tokyo 131-0045, Japan

ARTICLE INFO

Article history:

Received 25 June 2015

Revised 14 August 2015

Accepted 19 August 2015

Available online 28 August 2015

Keywords:

Orbital phase

Frontier orbital theory

Hydroamination

Catalysis

Organolanthanide

ABSTRACT

The frontier orbital theory is applied to investigate an organolanthanide-catalyzed reaction at the electronic level, using hydroamination/cyclization reactions of primary aminoalkynes. The insertion of the alkyne functionality into the Ln–N bond in $\text{Cp}_2\text{LnNH}(\text{CH}_2)_3\text{C}\equiv\text{CH}$ involved in the turnover-limiting cyclization step is found to be favored by the phases of HOMO of $\text{HC}\equiv\text{C}(\text{CH}_2)_3\text{NH}^-$ and LUMO of closed-shell Cp_2Ln^+ (Ln = La, Lu) or the LUMO+2 of excessive spins of open-shell Cp_2Sm^+ . The LUMO and LUMO+1 of Cp_2Sm^+ are 4f orbitals contracted too much to effectively overlap with HOMO of the counterpart. The HOMO–LUMO/LUMO+2 overlaps are visually shown and numerically confirmed to increase in the order of Ln = La < Sm < Lu in agreement with the observed turnover frequency.

© 2015 Elsevier Ltd. All rights reserved.

Introduction

The chemistry of lanthanide catalysis has made much progress.¹ Computational studies have contributed to our understanding of the general mechanisms and complemented experimental developments.² Marks and co-workers^{3–5} pioneered the use of lanthanides (Ln) for hydroamination and employed computational investigation in parallel with synthetic developments.

A catalytic cycle for organolanthanide-catalyzed hydroamination/cyclization of aminoalkynes (Scheme 1) was experimentally proposed for Ln = Sm and Cp^* (pentamethylcyclopentadienyl) and computationally supported for Ln = Sm and Cp (cyclopentadienyl) in place of Cp^* .⁵ The activated catalyst is generated from the reaction of the aminoalkyne with the precatalyst $\text{Cp}_2\text{SmCH}(\text{TMS})_2$. The alkyne functionality is inserted into the Ln–N(amido) bond in the rate-limiting step. The subsequent Ln–C protonolysis yields the enamine product and regenerates the activated catalyst to close the catalytic cycle. The computed hydroamination/cyclization energetic barriers were found in agreement with the observed catalytic activities low for La, modest for Sm, and high for Lu,³ which was understood in terms of Ln ion size.⁵

In this Letter, we disclose some essential aspects of the mechanisms of the hydroamination/cyclization reactions of

aminoalkynes, including the origin of the effect of lanthanide ion on the reaction rate. Very recently, we successfully applied the frontier orbital theory⁶ well established in organic reactions to transition metal mediated reactions to gain new insight to the Suzuki–Miyaura cross-coupling reactions⁷ and the olefin metathesis reaction.⁸ The success encourages us to apply the theory to the organolanthanide-mediated reactions, that is, hydroamination.

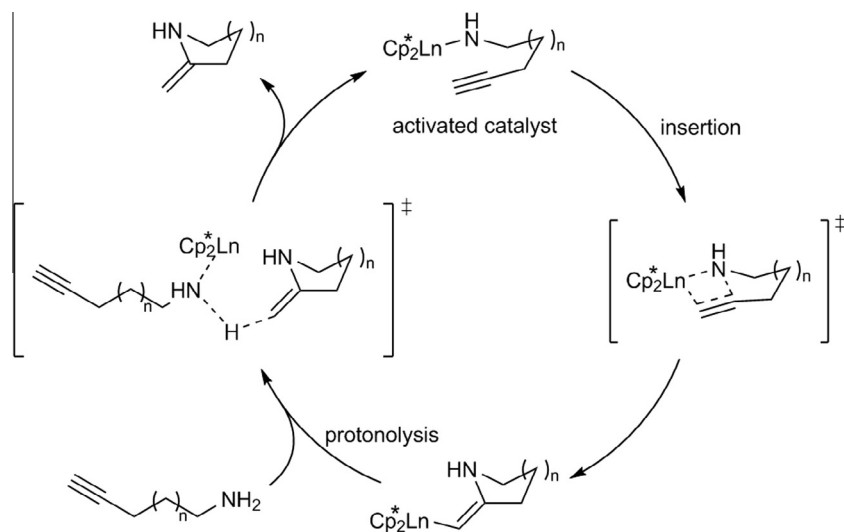
Results and discussion

Lanthanides (Ln) tend to be Ln^{3+} in the complexes.⁹ The electron configuration $[\text{Xe}] 6s^2 5d^0 4f^6$ of the samarium atom in the ground state formally changes into $[\text{Xe}] 4f^5$ of the Sm^{3+} ion. In the Cp_2SmX complexes the Sm atom donates one electron to each of two cyclopentadienyl (Cp) and the ligand (X). According to the Hund rule,¹⁰ five 4f-orbitals are occupied by excessive five α -spins with the remaining two f-orbitals unoccupied. In the ground state, Sm^{3+} has an open-shell electronic structure. The spin-multiplicity is sextet with all spin density (5.0) on the Sm atom. All open-shell calculations here use separate orbitals for the α and β spins.

The first step of the catalytic cycle is the C–N bond formation or the insertion of the C=C bond of the alkyne into Ln–N bond (Scheme 1). The $\text{HC}\equiv\text{C}(\text{CH}_2)_3\text{NH}^-$ and Cp_2Sm^+ parts are supposed to interact with each other at the transition state. The frontier orbital of $\text{HC}\equiv\text{C}(\text{CH}_2)_3\text{NH}^-$ is the HOMO because all the molecular orbitals lie high enough in energy due to the negative charge for

* Corresponding author. Tel./fax: +81 3 5841 4733.

E-mail addresses: inagaki@isc.chubu.ac.jp, finagaki@mail.ecc.u-tokyo.ac.jp (S. Inagaki).



Scheme 1. Catalytic cycle.

this part to be the electron donor. In the sextet state of Cp_2Sm^+ , two vacant 4f-orbitals are found to be the LUMO and LUMO+1 (Fig. 1). The 4f-orbitals are contracted too much¹³ (on the left-hand side of Fig. 1) relative to 5d and 6s orbitals to effectively overlap with the HOMO. It follows that the most important orbital is the next lowest LUMO+2 for the α -spin (abbreviated here as α -LUMO+2), which is a 5d, 6s, or hybrid orbital.

For the β -spins, the vacant 4f orbitals of Cp_2Sm^+ corresponding to α -LUMO and α -LUMO+1 are found to be LUMO+1 and LUMO+2. The β -LUMO is very similar in shape to α -LUMO+2. However, the β -LUMO energy (-0.050 au) is higher than α -LUMO+2 energy (-0.060 au). The HOMO–LUMO interaction for β -spins is less important than the HOMO–LUMO+2 interaction for α -spins.

In Figure 1, we depict¹¹ the overlap between α -HOMO of the closed-shell $\text{HC}\equiv\text{C}(\text{CH}_2)_3\text{NH}^-$ and α -LUMO+2 of the open-shell Cp_2Sm^+ in the sextet state at the transition structure.¹² The α -HOMO of $\text{HC}\equiv\text{C}(\text{CH}_2)_3\text{NH}^-$ has large amplitudes on the nitrogen atom and the terminal carbon atom (on the right-hand side in

Fig. 1). The α -LUMO+2 of Cp_2Sm^+ is a 5d orbital of Sm a little hybridized with 6s orbital (on the left-hand side in Fig. 1). The α -HOMO and α -LUMO+2 interact with each other in a cyclic manner (in the middle of Fig. 1). The α -LUMO+2 overlaps in phase with the α -HOMO at the nitrogen atom and the terminal carbon atom. The in-phase overlappings at both sites mutually strengthen the orbital interaction to stabilize the transition state of the cyclization of the $\text{HC}\equiv\text{C}(\text{CH}_2)_3\text{NH}^-$. The organolanthanide-mediated hydroamination has a feature of the cyclic orbital interaction favored by the orbital phase common with the well-known pericyclic reactions and with the transition-metal mediated Suzuki–Miyaura cross-coupling reactions⁷ and olefin metathesis reactions.⁸

The cyclization is taken as an intramolecular nucleophilic addition to an alkyne supported on the Sm atom in the complex. The HOMO of $\text{HC}\equiv\text{C}(\text{CH}_2)_3\text{NH}^-$ looks like the HOMO of an in-plane homo-1-azaallyl anion composed of a lone pair of the anionic nitrogen and the π bond between the carbon atoms. In fact, there

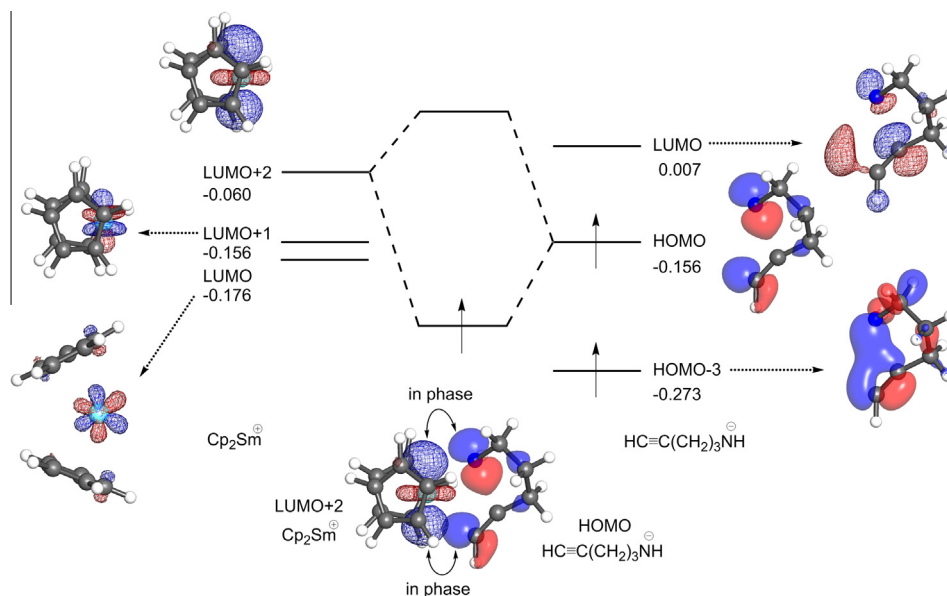


Figure 1. The in-phase overlappings between LUMO+2 of Cp_2Sm^+ and HOMO of $\text{HC}\equiv\text{C}(\text{CH}_2)_3\text{NH}^-$ at the transition state of hydroamination/cyclization process and the orbitals close in energy to the frontier orbitals. The occupied orbitals and the unoccupied orbitals are displayed in the transparent and mesh modes, respectively.

Download English Version:

<https://daneshyari.com/en/article/5268303>

Download Persian Version:

<https://daneshyari.com/article/5268303>

[Daneshyari.com](https://daneshyari.com)