アカデミックプログラム［B講演］ | 10. 有機化学—有機金属化合物：口頭B講演

2024年3月19日(火) 15:55 ~ 16:55 E1111(11号館 [1階] 1111)

[E1111-2vn] 10. 有機化学—有機金属化合物

座長：渕辺 耕平

英語
15:55 ~ 16:15
[E1111-2vn-01]
低原子価ニオブ錯体を触媒とするアルキンとシクロプロペンの [2+2+1]-環化付加反応による多置換シクロペンタジエン誘導体の合成

○秋山 拓弥[1]、真島 和志[2]、草本 哲郎[1]、劔 隼人[1] (1. 大阪大学大学院基礎工学研究科、2. 大阪大学大学院薬学研究科)

英語
16:15 ~ 16:35
[E1111-2vn-02]
Enantioselective [3+2] Annulation of Aromatic Aldimines with Alkynes via C−H Activation by Half-Sandwich Scandium Catalyst

○Aniket Mishra[1], Masayoshi Nishiura[1], Zhaomin Hou[1] (1. RIKEN CSRS)

英語
16:35 ~ 16:55
[E1111-2vn-03]
Efficient and Selective Synthesis of Sterically Hindered Secondary Amines by Rare-Earth-Catalyzed Sequential Imidoyl C-H Alkylation and Hydrosilylation of Aldimines

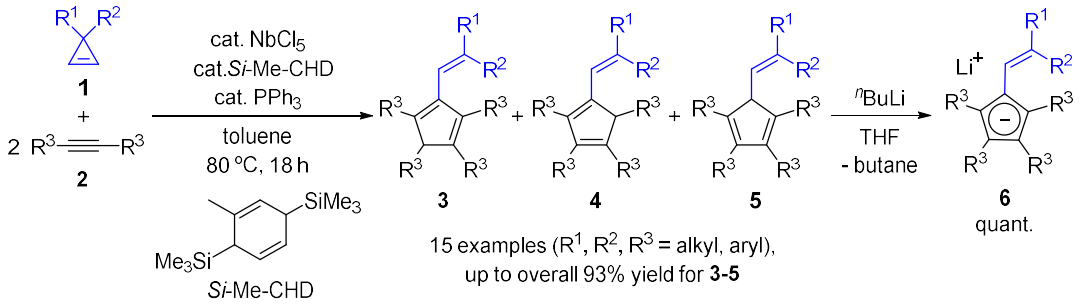
○Zhou Sun[1,2], Murahashi Nishiura[2], Feng Xue Cong[2], Tetsuro Murahashi[1], MIn Zhao Hou[2] (1. Tokyo Institute of Technology, 2. Riken)

Synthesis of Multi-substituted Cyclopentadiene Derivatives from 3,3-Disubstituted Cyclopropenes and Internal Alkynes Catalyzed by Low-valent Niobium Complexes

([1]*Graduate School of Engineering Science, Osaka University*, [2]*Graduate School of Pharmaceutical Science, Osaka University*) ○Takuya Akiyama,[1] Kazushi Mashima,[2] Tetsuro Kusamoto,[1] Hayato Tsurugi[1]

Keywords: Niobium; Cyclopentadiene; Cycloaddition; Alkyne Complex; Cyclopropene

Cyclopentadienes are the important class of carbocyclic compounds due to their applicability as cyclopentadienyl (Cp) ligands for organometallic complexes. Transition metal-catalyzed [2+2+1]-cycloaddition reactions of two simple alkynes and one carbene precursor are a powerful tool for synthesizing a wide variety of multi-substituted cyclopenadienes in atom- and step-economical manners, though suitable carbene precursors are still limited in this catalytic transformation.[1] Herein, we report an unprecedented [2+2+1]-cycloaddition reaction of 3,3-disubstituted cyclopropenes **1** and two equiv. of dialkyl/diarylacetylenes **2** leading to multi-substituted cyclopentadienes **3**－**5** as an isomeric mixture of the cyclopentadiene moiety, where a combination of an *in situ*-generated low-valent niobium species and PPh_3 exhibits high catalytic activity. ^{1}H NMR monitoring of the reaction products during the cyclopentadiene formation revealed that the reaction provides **4** and **5** as initial products, and subsequent proton migration *via* 1,5-sigmatropic hydrogen shift results in a thermodynamically controlled ratio of **3**/**4**/**5** in the reaction mixture. An isolated mixture of **3**－**5** is converted to lithium cyclopentadienide **6** as a sole product by treating with *n*-butyllithium in THF. The reaction mechanism of this unprecedented catalytic reaction was clarified by DFT calculation. The initial step is a formation of cyclopropane-fused metallacyclopentenes *via* 1,2-insertion of **1** into (η^2-alkyne)niobium species, and subsequent ring-opening of the fused cyclopropene ring provides niobium dienylcarbene species. Enyne metathesis of the niobium dienylcarbene species with the second alkyne forms metallacyclohexadiene whose reductive elimination after or without 1,5-proton transfer gives **4** or **5** as the products. We will disclose an applicability of the lithium cyclopentadienide for (cyclopentadienyl)metal complexes.



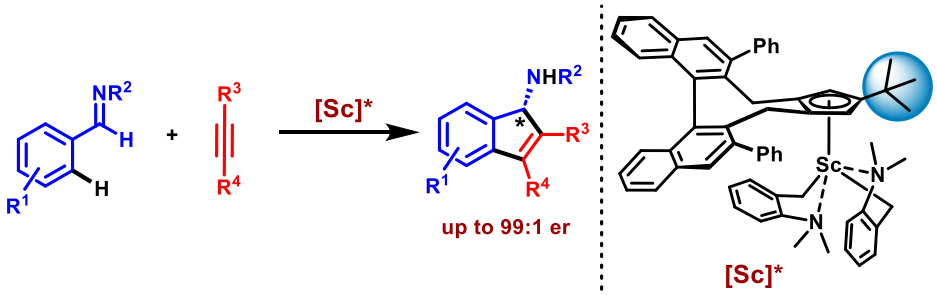
1) Frei, A. *Chem. Eur. J.* **2019**, *25*, 7074.

Enantioselective [3+2] Annulation of Aromatic Aldimines with Alkynes via C−H Activation by Half-Sandwich Scandium Catalyst

([1]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science*)
○Aniket Mishra,[1] Masayoshi Nishiura,[1] Zhaomin Hou[1]
Keywords: C–H activation, Annulation, Scandium, Rare-earth-metal, Asymmetric synthesis

Chiral 1-aminoindenes and its derivatives are important components in a wide array of natural products, pharmaceuticals, bioactive molecules, and functional materials. Therefore, the development of efficient protocols for the asymmetric synthesis of chiral 1-aminoindenes bearing a stereodefined amino functionality is of great interest and much importance. Ideally, formal asymmetric [3+2] annulation of aldimines with alkynes *via* the catalytic C–H activation represents the most straightforward and 100% atom-efficient route for the construction of densely functionalized chiral 1-aminoindenes. However, such an approach has remained unsuccessful, presumably due to the lack of suitable chiral catalysts. Recently, we have found that half-sandwich rare-earth-alkyl complexes can serve as efficient catalysts for the [3+2] annulation of aldimines and alkenes via C–H activation.[1] These studies invoked us to examine the feasibility of the asymmetric annulation of aldimines with alkynes by using chiral half-sandwich rare-earth-alkyl catalyst.

Herein, we report for the first time the enantioselective [3+2] annulation of a wide range of aldimines with internal alkynes via *ortho*- aryl C(sp^2)–H activation by a novel chiral half-sandwich scandium complex derived from a *tert*-butyl substituted chiral binaphthyl-bearing Cp. This protocol offers an efficient and selective route for the synthesis of a new family of chiral 1-aminoindenes in high yields with high regio- and enantioselectivity. Intriguingly, attractive noncovalent interaction such as C–H···π interaction plays a crucial role for determining the high level of enantioselectivity in an unprecedented manner, established by the DFT studies.



1) (a) X. Cong, G. Zhan, Z. Mo, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2020**, *143*, 5531. (b) A. Mishra, X. Cong, M. Nishiura, Z. Hou, *J. Am. Chem. Soc.* **2023**, *145*, 17468.

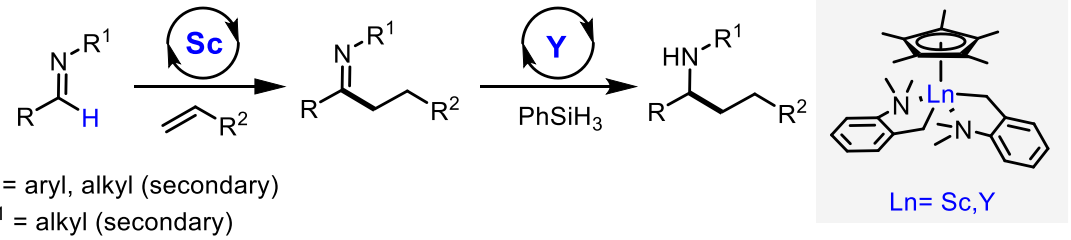
Efficient and Selective Synthesis of Sterically Hindered Secondary Amines by Rare-Earth-Catalyzed Sequential Imidoyl C-H Alkylation and Hydrosilylation of Aldimines

([1]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science,* [2]*Organometallic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, 2-1 Hirosawa, Wako, Saitama 351-0198*) ○Zhou Sun[1], Masayoshi Nishiura [1,2], Xuefeng Cong[1], Zhaomin Hou [1,2]

Keywords: *C-H alkylation, aldimines, rare-earth catalyst, hydrosilylation*

Sterically Hindered Secondary Amines are an important class of compounds that constitute the major body of bioactive natural products and pharmaceuticals[1]. The catalytic imidoyl C-H alkylation of aldimines with alkenes is an effective way to construct diverse sterically hindered ketimines which after hydrosilylation reaction can be converted to corresponding secondary amines. However, such transformation has remained a challenge to date because of the lack of suitable catalysts[2-3]. Here we report for the first time sequential imidoyl C-H alkylation of aldimines with alkenes followed by hydrosilylation of aldimines by half-sandwich rare-earth catalysts.

This protocol offers a straightforward and step-economical route for the synthesis of a series of sterically hindered secondary amines from easily accessible aliphatic or aromatic aldimines and alkenes (Fig.1). When R= secondary alkyl or aryl, R^1=secondary alkyl, imidoyl C-H alkylation of aldimines with styrenes exclusively afforded corresponding ketimines through the 2,1-insertion of a styrene unit by half-sandwich scandium catalysts and then after yttrium catalyzed reduction reaction can convert to different sterically hindered secondary amines, featuring excellent yields (70%-86%), broad substrate scope, high chemo- and regioselectivity under simple reaction conditions.



R = aryl, alkyl (secondary)
R^1 = alkyl (secondary)

Fig.1 Rare-Earth-Catalyzed Sequential Imidoyl C-H Alkylation and Hydrosilylation of Aldimines

References:

[1] R. N. Salvatore, C. H. Yoon, K. W. Jung, *Tetrahedron* **2001**, *57*, 7785 – 7811.

[2] X. Cong, Q. Zhuo, N. Hao, Z. Mo, G. Zhan, M. Nishiura, Z. Hou. J. Am. Chem. Soc., **2022**, *61*, e202

[3] Dixneuf. P. H. et al, *ACS Catal.* **2011**, 1, 122.