A Journal of the Gesellschaft Deutscher Chemiker

Angewandte International Edition GDCh Chemie

www.angewandte.org

Accepted Article

Title: (NHC)NiIIH-Catalyzed Cross-Hydroalkenylation of Cyclopropene with Alkyne: A Straight Forward Cyclopentadiene Synthesis by NHC-NiII Assisted C-C Rearrangement.

Authors: Jian-Qiang Huang and Chun Yu Ho

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201901255
Angew. Chem. 10.1002/ange.201901255

Link to VoR: http://dx.doi.org/10.1002/anie.201901255
http://dx.doi.org/10.1002/ange.201901255

WILEY-VCH

10.1002/anie.201901255

WILEY-VCH

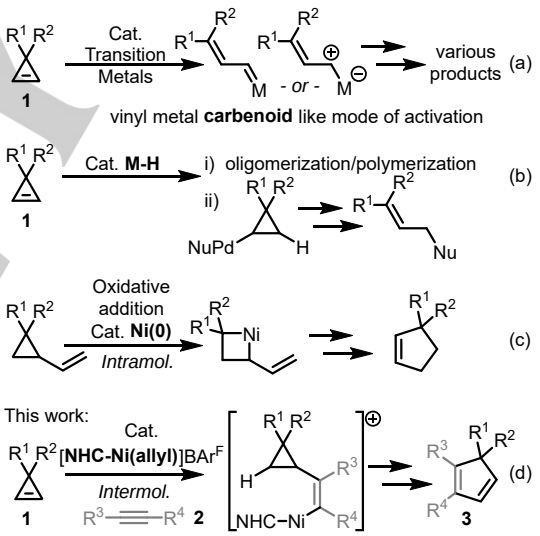
(NHC)Ni^{II}H-Catalyzed Cross-Hydroalkenylation of Cyclopropene with Alkyne: A Straight Forward Cyclopentadiene Synthesis by NHC-Ni^{II} Assisted C-C Rearrangement.

Jian–Qiang Huang[a,b], Chun–Yu Ho*[a]

Abstract: Cross-hydroalkenylation-rearrangement cascade (HARC) that using cyclopropene **1** and alkyne **2** as substrate pairs was first achieved by using a set of new [NHC-Ni(allyl)]BAr^F catalysts. By controlling the NHC-Ni^{II}H relative insertion reactivity with **1** and **2**, a broad scope of cyclopentadiene **3** was obtained highly selectively for the first time. The new NHC-Ni^{II} catalyst structural features were found as the keys for the success. The mild condition employed may serve as an entry for exploring NHC-Ni^{II} assisted vinylcyclopropane rearrangement reactivity.

Cyclopropene **1** is an important building block in organic synthesis, significant advances for its synthesis have been made recently by new transition metal catalysts and innovations. Other than the use of traditional methods,[1] catalysts like Au[2], Rh,[3] Cu,[4] Zn[5] Pt[6] and Pd[7] are particularly useful in ring opening reactions of **1**.[8] The intermediates, such as the reactive vinyl metal carbenoids and the cyclopropane ions, were often trapped by other nearby functional groups on the skeleton or external nucleophiles (Scheme 1a). That provides a general route to substituted furans, pyrans and acyclic products. Transition metal hydride catalysts or their equivalents[9] could potentially be one of the most ideal approaches for cyclopropene functionalization too, since it could insert to the olefin and allow subsequent insertions of various reaction partners easily. However, their use in selective transformation of **1** is reported rarely.[7] A number of other possible reactivity of **1** with transition metal hydride, leading to unfavorable **1** consumption, have severely limited the progress of the cross-reaction development. With either too high insertion activity of **1** or competing pathways from other reaction partners such as alkyne **2**, the non-selective oligomerization or homo-reaction reactivity is often dominated (Scheme 1bi). Moreover, other possible rearrangements were reported as one of the possible pathways for allyl-Nu formation, and that made the hydride approach even more complicated (Scheme 1bii). As a consequence, highly selective cross-transformations of **1** by transition metal hydride catalyst and external π-systems[2b, 3d, 4, 10] remains elusive. Oxidative addition followed by rearrangement or trapping is still dominating the field in Ni catalyzed 3-member ring opening (Scheme 1c).[11], [12]

Herein, a cross-**h**ydro**a**lkenylation-**r**earrangement **c**ascade (HARC) of **1** and **2** was first achieved by using a new set of [NHC-Ni(allyl)]BAr^F catalyst (Scheme 1d). Unlike the cross-hydroalkenylation of two different alkenes,[9b, 13],[14] it provides a highly efficient access to synthetically valuable, functionalized cyclopentadienes **3** rather than gem-olefins. Instead of using oxidative addition condition for 3-member ring opening by Ni(0) in Scheme 1c, the CC bond cleavage was assisted possibly by NHC-Ni^{II} in a subsequent rearrangement at mild condition. In sharp contrast to the typical **1** and **2** reactivity with metal hydride as described in Scheme 1b, chemoselective insertion of **1** and **2** was achieved, where a Pd-cyclopropyl type of rearrangement was avoided and two new CC bonds were formed at cyclopropene C_1 and C_3-positions. When compared to the other transition metal catalyst systems that rely on vinyl metal carbenoids[10] in Scheme 1a, unparalleled reactivity and new scope were observed. The above, together with labelling experiments, suggested the NHC-Ni^{II}-cyclopropanyl and the later on NHC-Ni^{II}-vinylcyclopropenyl species might be the key possible intermediates that account for the observations.



Scheme 1. Functionalized cyclopentadiene synthesis.

Our study commenced with cyclopropene **1a** and terminal alkyne **2a** by using a sterically bulky [IPr-Ni(allyl)]BAr^F] catalyst reported in diene cycloisomerization[15] and hydroalkenylation[13a] with octene (Table 1). It is because we suspected that 1) the use of sterically bulky NHC might mitigate the high reactive of **1** and **2** towards Ni^{II}H and provide chemoselective insertion; and 2) a possibly more selective insertion might let the HARC under control. While the use of either Ni(0)[16][11b, 17] or Ni(allyl)BAr^F favored either nonselective oligomerization or dimerization (entries 10-12), **1a** and **2a** were converted into the desired cyclopentadiene **3aa** regioselectively and highly atom-economically in the presence of [IPr-Ni(allyl)]BAr^F] catalyst for the first time (entry 2).[11a, 11b] This HARC was done simply at low catalyst loading, at ambient condition and without adding stoichiometric amount of additive. A slightly higher alkyne to

[a] Dr. J.-Q. Huang, Prof. Dr. C.-Y. Ho*
Shenzhen Grubbs Institute, Department of Chemistry, Southern University of Science and Technology (SUSTech), China
E-mail: jasonhcy@sustc.edu.cn
[b] Department of Chemistry and Molecular Sciences, Wuhan University, China

Supporting information for this article is given via a link at the end of the document.

10.1002/anie.201901255

cyclopropene ratio was proved effective to suppress undesired **1a** consumption (entry 2), and the choice of ligand structure was found very important. Among the NHCs examined (Figure 1), 6-SIPr (**L6**) and IPent (**L4**) provided the best result while the IMes and 7-SIPr provided the worst (entries 1-7), thus indicating that the desired reactivity was brought by optimal NHC steric bulkiness, either by the size of NHC core or N-aryl substituents. The effect of steric increment method choice was dramatic only when a linear unsubstituted terminal alkyne **1b** was used. At here, moderate yield of **3ab** was obtained even when a large excess amount of **2b** (6 equiv) was used by having **L6** as ligand, however, just 1:2 substrate ratio at 1 mol% [**L4**-Ni(allyl)]BAr^F catalyst could provide up to 82% yield (entries 8 and 9).

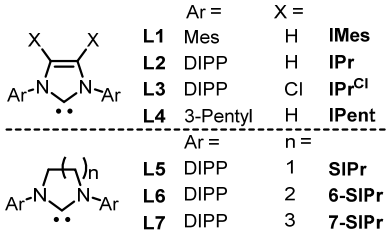
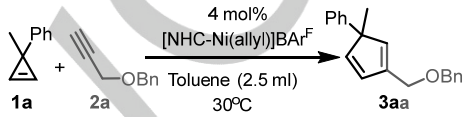


Figure 1. NHC structures employed in this work.

The fine-tuned $Ni^{II}H$ reactivity with **1**, which was brought by NHC optimization, came with also a broad scope of **2** (Table 2). It provided a new general access to functionalized **3** in one step simply at mild reaction condition (30°C), low substrate ratio (as low as equimolar) and low catalyst loading (1-4 mol%). It complements to a few shortcomings by the intramolecular approaches,[18] tailor-made ynamides with Au vinyl carbenoids,[10, 19] cycloaddition,[20] and approaches that using stoichiometric amount of organometallic reagents.[21] High yield, functional group compatibility and regioselectivity (up to 46:1, > 20:1 in general) were noted in cases with commercially available or simple terminal **2** (Set 1-3). A vast number of general and functionalized acetylenes, both sterically demanding (Set 2, Y = TMS, tBu, Cy, CH_2Cy, aryl) and electronic activated (Set 3, Y = acyl, ferrocenyl, 3-thiophen, ester) were also identified as good substrates for the first time. Lower yield was noted in some electron-poor acetylenes, which might be related to their insertion reactivity (Y = acyl and ester). Yet, their product regioselectivity remained high (> 20:1). This HARC system is also compatible with the internal alkynes (Set 4, both neutral and hetero). This allowed the preparation of higher substituted and hetero-substituted **3** for joining other common transformations. The fine-tuned NHC-$Ni^{II}H$ insertion reactivity is also compatible with other commonly employed **1** in the literature. Symmetric and unsymmetric, dialkyl and diaryl, as well as spiro-substitution patterns on **1** were also accepted in this new system (Set 5), hence indicating that the desired reactivity was not limited by steric bias from Ph and Me. Notably, by making use of a) the higher reactivity of terminal alkyne than alkene and internal alkyne; as well as b) the slightly lower reactivity of catalyst with **L6** than **L4**, a highly chemoselective formation of **3** was achieved even in the presence of nearby π-systems competitions (Set 6, internal alkynes and alkenes).[2b] In addition, a low terminal alkene isomerization (1-:2-alkene ratio) was observed, which was deemed facile under $Ni^{II}H$ conditions (Set 6, Z = O, NTs).[22] That was attributed to the choice of NHC employed, where the use of former hydroalkenylation catalyst with **L2** suffered from isomerization more than that of **L6** in Z = NTs. Interestingly, conjugated enyne was found also compatible to the system, which allowed the synthesis of triene (Set 6). Overall, **L6** was found suitable for structurally flexible substrates (e.g. **1** has mixed small alkyl and aryl, **2** has terminal propargylic X), while **L4** was found more suitable for substrates with lower structural flexibility (e.g. **1** & **2** have bulky substituents, like Y = Ph; R^1 = iPr; $R^1 = R^2$ = Ph or spiroskeleton; and internal **2**).[23]

Table 1 Screening NHC for desired $Ni^{II}H$, **1** and **2** relative insertion reactivity.[a]

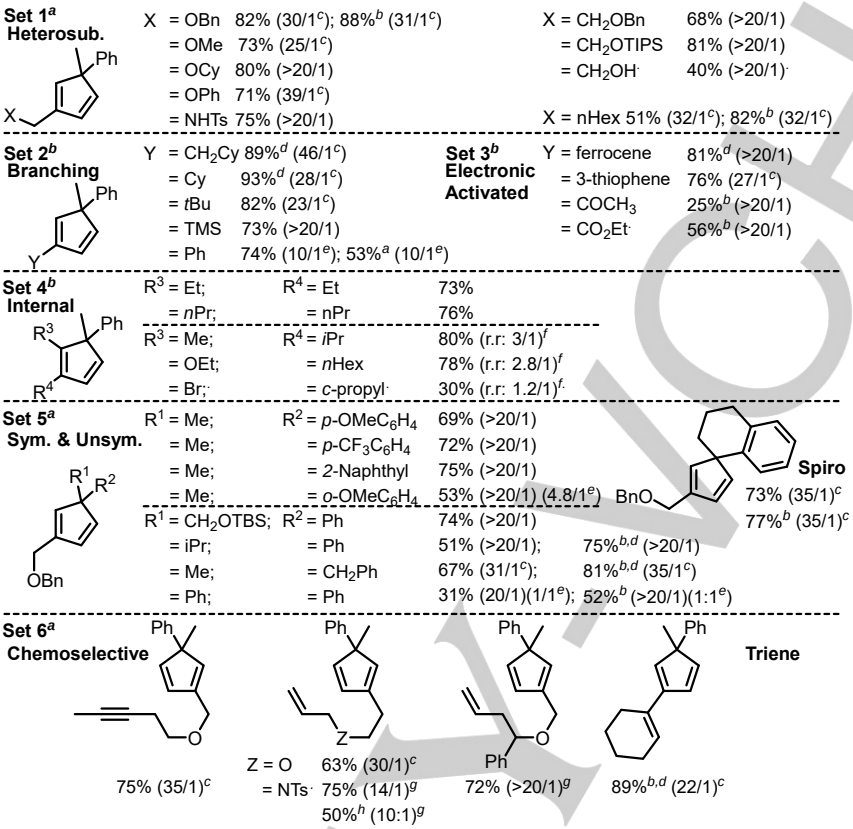


	2	Condition NHC =	Yield (3)	Yield[b]
1	2a	IMes (L1)	23%	50%
2		IPr (L2)	56%; 35%;[c] 61%[d]	10%
3		IPr^{Cl} (L3)	64%	15%
4		IPent (L4)	88%; 76%[e]	<1%
5		SIPr (L5)	63%	15%
6		6-SIPr (L6)	82%	<1%
7		7-SIPr (L7)	25% (60%)[f]	30%
8	2b[g]	6-SIPr (L6)	46%; 52%[h]	30%
9		IPent (L4)	84%; 82%[i]	<1%
10	2a/b	Only $Ni(COD)_2$	–	–[j]
11		L4 + $Ni(COD)_2$	–	–[j]
12		No NHC	–	–[j]

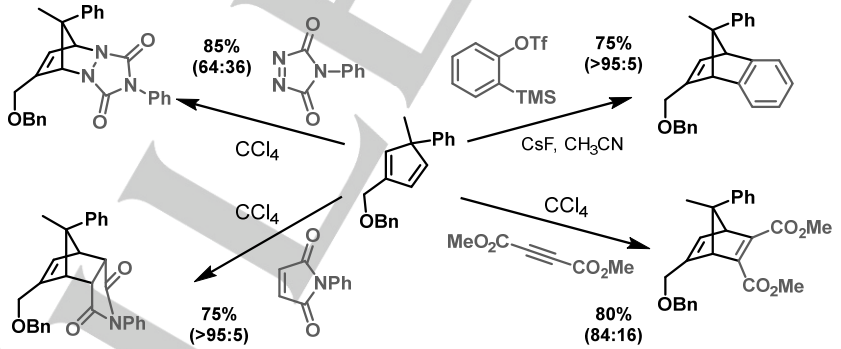
[a] Screening condition: Substrate (**1a**: **2** = 1: 2) was added to 4 mol% [NHC-Ni(allyl)BAr^F] catalyst (0.02 mmol) with 16 mol% 1-octene in toluene and stirred for 1 hr at 30°C. Conversion of **1a** and **2** were 100% except otherwise indicated. Yield was determined by ^{1}H NMR. [b] Yield of low MW oligomers estimated by GCMS. [c] **1**: **2** = 1: 1. [d] An extra 1 equiv of **2a** was added after 0.5 h. [e] 0.5 mol% catalyst (0.025 mmol), **1**:**2** = 1:1.2. [f] conversion of **1a**. [g] **2b** = 1-Octyne. [h] 6 equiv of **2b** was added. [i] 1 mol% cat., 1 mL toluene, 3 hrs. [j] Sticky gel was obtained, yield of **3** was not determined.

The robust condition that we obtained also allowed us to carry out gram-scale HARC reaction without difficulty. By using 0.5 mol% catalyst with **L4** (Table 1, entry 4), 1.05 g of **3aa** was prepared which prompted us to explore the product reactivity. The product was found compatible with a number of (hetero) Diels-Alder reactions (Scheme 2).[24] High yield, reactivity and selectivity were obtained by slightly modified conditions for simpler cyclic dienes. Functionalized bicycle[2.2.1]heptanes and derivatives were obtained in 2 steps from **2a**, which are common units in many drug candidates and bioactive compounds.

Table 2 Scope of the cyclopentadiene **3** synthesized by [NHC-Ni(allyl)]BAr^F catalyzed HARC.[a]



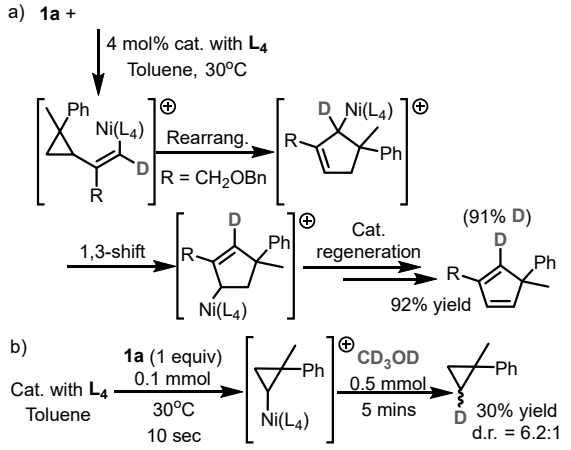
Cross-HARC condition: **1**:**2** = 1:2, at 30°C. Isolated yield of the preferred regioisomer **3** was shown. Values in parenthesis are the regioselectivity of **3**, which was determined by ^{1}H NMR except otherwise indicated. [a] Method A: [**L6**-Ni(allyl)]BAr^F (4 mol%, 0.02 mmol) in 3 mL toluene for 1 hr. [b] Method B: [**L4**-Ni(allyl)]BAr^F (1 mol%, 0.005 mmol) in 1 mL toluene for 3 hrs. [c] By GCMS (ratio of **3**: others with same MW); [d] Equimolar ratio of **1** and **2** was used. [e] Conformational isomers ratio. [f] Ratio of regioisomers. [g] > 20/1 regioisomer ratio. Values in parenthesis are the ratio of **3** with 1-:2-alkene (E/Z mixture). [h] By Method A, except **L2** (IPr) was used instead of **L6**.



Scheme 2. Convenient route for substituted bicycle[2.2.1]heptane derivatives. *Syn:Anti*-product ratio was in parenthesis. The contrasteric structures obtained were assigned by a comparison that used 5-methyl-5-phenylcyclopentadiene.[25]

At this stage, the keys for the straightforward synthesis of **3** with broad scope were attributed mainly to optimal insertion reactivity of **1** and **2** by their steric interactions with **L4** / **L6**-Ni^{II}, and to the high rearrangement reactivity of vinylcyclopropane assisted by NHC-Ni^{II}, both under mild condition (Scheme 3). One of the possible reaction sequences might involve a NHC-Ni^{II} directed selective cross-hydroalkenylation of **1** with **2**. Here, a chemoselective insertion of **1** occurred (favored by ring-strain release),[8] followed by a fast regioselective insertion of **2**, rather than a homo-insertion of **1** (by steric interaction of **1** with bulky NHCs as depicted in Table 1) or premature ring-opening in Pd. After a NHC-Ni^{II} assisted vinylcyclopropane rearrangement at just 30°C as compared to Scheme 1c (alkenyl-Ni^{II} activation),[11b, 17, 26] NHC-Ni^{II}-allyl 1,3-shift[27] and catalyst regeneration by a β-H elimination/transfer, [27c-e] the desired product **3** was obtained. In this way, this HARC could occur without slow addition of substrates, and fairly free from non-selective oligomerization competitions of either **1** or **2**. D-labelling experiments support the

hypothesis in part: i) < 4% D exchange was observed when D_1-**2a** was used and produced the corresponding D-labelled **3aa** successfully (Scheme 3a). This supported that NHC-Ni^{II}-acetylene species was not involved. ii) Mono-deuteriated cyclopropane was obtained by an early CD_3OD quenching (Scheme 3b). This suggested the insertion of **1** to catalyst is fast and the NHC-Ni^{II}-cyclopropyl rearrangement analogous to the Pd or Au systems is relatively slow. Overall, this new mode of reactivity and selectivity expanded the scope and efficiency of **3** preparation significantly, which is a persistent challenge in many systems.



Scheme 3. Labelling experiment and working hypothesis. Postulated structures are in brackets at this stage.

In conclusion, a highly efficient cross-HARC of **1** and **2** was first established by manipulating the relative insertion reactivity of **1**, **2** and NHC-Ni^{II}. Unlike the hydroalkenylation studies that using [NHC-Ni(allyl)]BAr^F with two alkenes, cyclic dienes rather than gem-olefins were obtained by subsequent rearrangements for the first time and just at fairly mild condition. This route provides versatile access to functionalized **3** and bicycle[2.2.1]heptane derivatives, both are difficult to obtain expediently and atom-economically with this broad substrate scope before. This report also represents the first applications of **1** and **2** with [NHC-Ni(allyl)]BAr^F, which broadens the use of those easily accessible substrates in organic synthesis. The new reactivity preference offered new insights for achieving other applications and rearrangements by NHC-T.M. hydrides.

Experimental Section

Standard procedure: To 0.005-0.020 mmol catalyst mixture in toluene (1-2 mL, by stock solution), an indicated amount of **1** and **2** toluene premixed solution (0.5 mmol in 1 mL) were added in one-pot and stirred at 30°C for 1-3 hrs. A spatula of Na_2CO_3(s) was added after the reaction, and the mixture was diluted with 4 mL hexane and stirred in open air for 1 hr. Then it was filtered through a short plug of silica gel and rinsed with diethyl ether. The solvent was then removed under reduced pressure. Conversion of **1** and selectivity of **3** to other possible isomers were determined by ^1H NMR or GCMS (average of two runs). Product structures were confirmed by isolation.

Acknowledgements

CYH thanks R. H. Grubbs (Shenzhen Nobel Prize Scientists Laboratory Project C17213101), SZ research fund (JCYJ 20170817105041557) and NSFC (21602099). CYH and JQH thank Yang HU for substrate preparation.

Keywords: N-heterocyclic carbenes • hydroalkenylation • nickel • cyclopentadiene • cyclopropene • alkyne.

[1] a) M. S. Baird, *Chem Rev* **2003**, *103*, 1271; b) F. L. Carter, V. L. Frampton, *Chem Rev* **1964**, *64*, 497.

[2] a) C. Y. Wu, T. Horibe, C. B. Jacobsen, F. D. Toste, *Nature* **2015**, *517*, 449; b) F. Miege, C. Meyer, J. Cossy, *Chemistry* **2012**, *18*, 7810; c) M. S. Hadfield, A. L. Lee, *Chem Commun (Camb)* **2011**, *47*, 1333; d) M. S. Hadfield, J. T. Bauer, P. E. Glen, A. L. Lee, *Org Biomol Chem* **2010**, *8*, 4090.

[3] a) P. A. Wender, T. J. Paxton, T. J. Williams, *J Am Chem Soc* **2006**, *128*, 14814; b) X. Wang, A. Lerchen, C. G. Daniliuc, F. Glorius, *Angew Chem Int Ed Engl* **2018**, *57*, 1712; c) H. Zhang, K. Wang, B. Wang, H. Yi, F. Hu, C. Li, Y. Zhang, J. Wang, *Angew Chem Int Ed Engl* **2014**, *53*, 13234; d) F. Miege, C. Meyer, J. Cossy, *Angew Chem Int Ed Engl* **2011**, *50*, 5932.

[4] C. Song, L. Ju, M. Wang, P. Liu, Y. Zhang, J. Wang, Z. Xu, *Chemistry* **2013**, *19*, 3584.

[5] M. J. Gonzalez, J. Gonzalez, L. A. Lopez, R. Vicente, *Angew Chem Int Ed Engl* **2015**, *54*, 12139.

[6] J. Li, C. Sun, S. Demerzhan, D. Lee, *J Am Chem Soc* **2011**, *133*, 12964.

[7] I. Nakamura, G. B. Bajracharya, Y. Yamamoto, *J Org Chem* **2003**, *68*, 2297.

[8] G. Fumagalli, S. Stanton, J. F. Bower, *Chem Rev* **2017**, *117*, 9404.

[9] a) T. V. RajanBabu, *Chem Rev* **2003**, *103*, 2845; b) C. Y. Ho, L. S. He, C. W. Chan, *Synlett* **2011**, 1649; c) R. M. Ceder, A. Grabulosa, G. Muller, M. Rocamora, *Catal Sci Technol* **2013**, *3*, 1446; d) G. Hilt, *Chemcatchem* **2015**, *7*, 1639.

[10] X. Cheng, L. Zhu, M. Lin, J. Chen, X. Huang, *Chem Commun (Camb)* **2017**, *53*, 3745.

[11] a) G. Zuo, J. Louie, *Angew Chem Int Edit* **2004**, *43*, 2277; b) S. C. Wang, D. M. Troast, M. Conda-Sheridan, G. Zuo, D. LaGarde, J. Louie, D. J. Tantillo, *J Org Chem* **2009**, *74*, 7822; c) J. Terao, M. Tomita, S. P. Singh, N. Kambe, *Angew Chem Int Edit* **2010**, *49*, 144; d) T. Tamaki, M. Ohashi, S. Ogoshi, *Angew Chem Int Edit* **2011**, *50*, 12067; e) M. Shirakura, M. Suginome, *J Am Chem Soc* **2009**, *131*, 5060; f) L. Liu, J. Montgomery, *J Am Chem Soc* **2006**, *128*, 5348; g) T. Tamaki, M. Nagata, M. Ohashi, S. Ogoshi, *Chem-Eur J* **2009**, *15*, 10083; h) M. C. Martin, D. V. Patil, S. France, *J Org Chem* **2014**, *79*, 3030.

[12] a) K. Ogata, Y. Atsuumi, S. Fukuzawa, *Org Lett* **2010**, *12*, 4536; b) S. Saito, K. Maeda, R. Yamasaki, T. Kitamura, M. Nakagawa, K. Kato, I. Azumaya, H. Masu, *Angew Chem Int Edit* **2010**, *49*, 1830.

[13] a) W. H. Chen, Y. Li, Y. Chen, C. Y. Ho, *Angew Chem Int Edit* **2018**, *57*, 2677; b) X. Y. Lian, W. H. Chen, L. Dang, Y. C. Li, C. Y. Ho, *Angew Chem Int Edit* **2017**, *56*, 9048; c) C. Y. Ho, C. W. Chan, L. S. He, *Angew Chem Int Edit* **2015**, *54*, 4512.

[14] a) D. F. Fernandez, M. Gulias, J. L. Mascarenas, F. Lopez, *Angew Chem Int Edit* **2017**, *56*, 9541; b) L. J. Xiao, C. Y. Zhao, L. Cheng, B. Y. Feng, W. M. Feng, J. H. Xie, X. F. Xu, Q. L. Zhou, *Angew Chem Int Edit* **2018**, *57*, 3396; c) F. Strieth-Kalthoff, A. R. Longstreet, J. M. Weber, T. F. Jamison, *Chemcatchem* **2018**, *10*, 2873.

[15] S. Biswas, A. B. Zhang, B. Raya, T. V. RajanBabu, *Advanced Synthesis & Catalysis* **2014**, *356*, 2281.

[16] Ni(0) is known effective catalyst for vinylcyclopropAne opening by oxidative addition but not cyclopropene.

[17] H. R. Rounds, M. Zeller, C. Uyeda, *Organometallics* **2018**, *37*, 545.

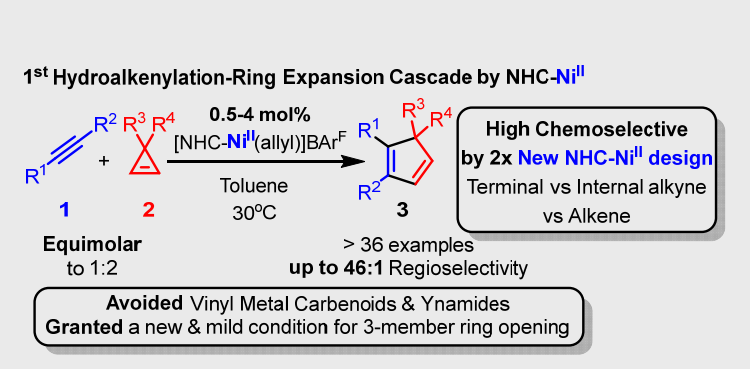
[18] a) J. H. Lee, F. D. Toste, *Angew Chem Int Edit* **2007**, *46*, 912; b) H. Funami, H. Kusama, N. Iwasawa, *Angew Chem Int Edit* **2007**, *46*, 909.
[19] a) S. Kramer, Y. Odabachian, J. Overgaard, M. Rottlander, F. Gagosz, T. Skrydstrup, *Angew Chem Int Edit* **2011**, *50*, 5090; b) E. Rettenmeier, A. M. Schuster, M. Rudolph, F. Rominger, C. A. Gade, A. S. K. Hashmi, *Angew Chem Int Edit* **2013**, *52*, 5880.
[20] Z. X. Fang, J. Q. Liu, Q. Liu, X. H. Bi, *Angew Chem Int Edit* **2014**, *53*, 7209.
[21] a) Z. F. Xi, P. X. Li, *Angew Chem Int Edit* **2000**, *39*, 2950; b) Z. F. Xi, Q. L. Song, J. L. Chen, H. R. Guan, P. X. Li, *Angew Chem Int Edit* **2001**, *40*, 1913.
[22] We were surprised to notice that the 1-alkene was not isomerized to 2-alkene under the Method A condition. However, part of the 1-alkene was isomerized when less bulky NHC was employed.
[23] The reason for why the **L6** is not good for 1-octyne case is unclear at this stage. Presumably, the heteroatoms on **2** might somehow involve in guiding the desired reactivity in Set 1.
[24] Wasserman, A. Diels-Alder Reactions; Elsevier: Amsterdam, 1965; p 114.
[25] M. Ishida, M. Itakura, H. Tashiro, *Tetrahedron Lett* **2008**, *49*, 1804.
[26] For a recent tandem hydrovinylation by Co catalyst: V. V. Pagar, T. V. RajanBabu, *Science* **2018**, *361*, 68.
[27] a) R. J. Ely, J. P. Morken, *Org Lett* **2010**, *12*, 4348; b) M. Holscher, G. Francio, W. Leitner, *Organometallics* **2004**, *23*, 5606; c) X. Hong, J. L. Wang, Y. F. Yang, L. S. He, C. Y. Ho, K. N. Houk, *Acs Catal* **2015**, *5*, 5545; d) Y. Gao, K. N. Houk, C. Y. Ho, X. Hong, *Org Biomol Chem* **2017**, *15*, 7131; Phosphorous ligand case: e) J. Joseph, T. V. RajanBabu, E. D. Jemmis, *Organometallics* **2009**, *28*, 3552.

.

10.1002/anie.201901255

WILEY-VCH

COMMUNICATION



*Jian-Qiang Huang, Chun–Yu Ho**

Page No. – Page No.

(NHC)Ni^{II}H-Catalyzed Cross-Hydroalkenylation of Cyclopropene with Alkyne: A Straightforward Cyclopentadiene Synthesis by NHC-Ni^{II} Assisted Rearrangement.

Hydroalkenylation-rearrangement cascade. Functionalized cyclopentadiene **3** was prepared by catalytic cross-hydroalkenylation-rearrangement cascade in high yield and step-economy. The keys for the success and broad substrate scope of cyclopropene **1** and alkyne **2** are the optimal insertion reactivity and high rearrangement reactivity enabled by the new NHC-Ni^{II} design under mild condition. Two new [NHC-Ni(allyl)]BAr^F catalysts were developed, they showed the potentials of NHC in tuning transition metal hydride reactivity towards the high reactivity of **1** and **2**. This discovery opens up new opportunities in NHC directing cascade, and expands the number of possible combinations significantly.