A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
International Edition
www.angewandte.org

Accepted Article

Title: Rh(II)- or Cu(I)-Catalyzed Formal Intramolecular Carbene Insertion into Vinylic C(sp2)-H Bond: An Access toward Substituted 1H Indenes

Authors: Jianbo Wang, Qi Zhou, Shichao Li, and Yan Zhang

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201709375
Angew. Chem. 10.1002/ange.201709375

Link to VoR: http://dx.doi.org/10.1002/anie.201709375
http://dx.doi.org/10.1002/ange.201709375

WILEY-VCH

Carbene Insertion

DOI: 10.1002/anie.200((will be filled in by the editorial staff))

Rh^{II}- or Cu^{I}-Catalyzed Formal Intramolecular Carbene Insertion into Vinylic C(sp^2)-H Bond: An Access toward Substituted 1*H* Indenes**

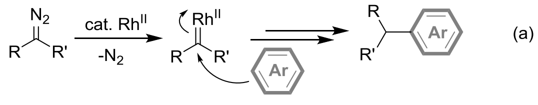
*Qi Zhou, Shichao Li, Yan Zhang, Jianbo Wang**

***Abstract**: A Rh^{II} or Cu^{I}-catalyzed formal intramolecular carbene insertion into vinylic C(sp^2)-H bonds is reported herein. This method provides straightforward access to 1H-indenes with high efficiency and excellent functional group compatibility. Mechanistically, the reaction is proposed to involve the following sequence: metal carbene formation, intramolecular nucleophilic addition of the double bond to electron-deficient carbenic carbon, dearomatization and finally 1,5-H shift.*

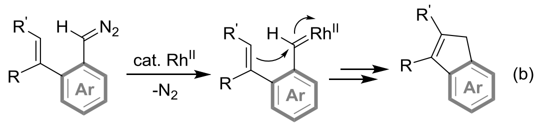
Transition-metal-catalyzed carbene insertion into C-H bonds represents one of the characteristic transformations of metal carbene species.[1] The previous studies for carbene insertion into C-H bonds have been focused in aliphatic C(sp^3)-H bonds. For example, Davies and co-workers have demonstrated remarkable regio- and stereoselectivities for intermolecular C(sp^3)-H bond insertions with donor-acceptor carbene precursors and chiral Rh(II) catalysts.[2] With Ru^{II}-porphyrin complexes as the catalysts, Che and co-workers have demonstrated the selective carbene insertion into primary C-H bonds of alkanes.[3] Pérez and co-workers reported a Ag-catalyzed carbene insertion into methane C-H bond in supercritical CO_2.[4] Transition-metal-catalyzed carbene insertion into C(sp^3)-H bonds is considered as an unique method for inert C(sp^3)-H bond functionalization, which has attracted significant attentions in recent years.

In addition to C(sp^3)-H bond insertions, carbene insertion into aromatic C(sp^2)-H bonds are also well-documented.[5] Mechanistically, aromatic C(sp^2)-H bond insertion is different from the corresponding C(sp^3)-H bond insertion: the former follows stepwise electrophilic substitution mechanism, while the latter usually proceeds through concerted insertion mechanism. For electron-deficient aromatic C-H bonds, formal C-H insertion may also follows a mechanism involving C-H bond metalation and carbene migratory insertion.[6] Regardless of the differences in reaction pathways, the carbene aromatic C(sp^2)-H bond insertions are well established as unique approaches for direct aromatic C-H bond functionalizations.[7] In the contrast, the insertion into vinylic C-H bonds by carbene remains much less developed, presumably attributed to the competing cyclopropanation of alkene as an uncontainable side reaction.[8]

Such side reaction may be minimized in intramolecular reactions. In this context, de Bruin and co-workers have recently reported the Co^{II}-catalyzed formal Co^{III}-carbene insertion into vinyl C-H bond for the synthesis of substituted 1*H*-indenes.[9] The reaction is proposed to proceed through a radical process. Interestingly, in their work $Rh_2(OAc)_4$ failed to catalyse the reaction, while the Cu^{I}-catalyzed reaction gave only poor results. Herein we demonstrate the highly efficient Rh^{II} or Cu^{I}-catalyzed intramolecular carbene insertions into vinylic C-H bond for the synthesis of substituted 1*H* indenes. Mechanistic studies indicate the reaction follows a stepwise pathway involving carbon cation intermediate, which is distinct from the radical process in de Bruin's Co^{III} carbene radical system.



Insertion into aromatic C(sp^2)-H bond



Insertion into vinylic C(sp^2)-H bond

Scheme 1. Formal Rh^{II} carbene insertion into C(sp^2)-H bond.

Since *N*-tosylhydrazones have been extensively explored as the precursors for in situ generation of non-stabilized diazo substrates,[10] we began our study with *o*-vinyl *N*-tosylhydrazone **1a** as the model substrate. When $Rh_2(OAc)_4$ was used as the catalyst in dichloroethane (DCE) at 100 °C, the expected vinylic C-H bond insertion product **2a** could be obtained in 38% isolated yield (Table 1, entry 1). Further experiments show that toluene is the optimal solvent. Carrying out the reaction at lower temperature led to decrease of the yields (Table 1, entries 4-6). The effect of bases was then examined and LiO^{t}Bu was found to afford optimal results (Table 1, entries 8-10).

Subsequently, a series of metal catalysts were screened with slightly decreased loading of LiO^{t}Bu (Table 1, entries 11-17). The highest yield was obtained by using $Rh_2(Oct)_4$ as the catalyst (Table 1, entry 12). It is noteworthy that CuI as a cheap catalyst could also exhibit good activity (Table 1, entry 16). Finally, control experiment suggested that in the absence of transition-metal catalyst, the reaction under otherwise identical conditions failed to give the product **2a** (Table 1, entry 18).

Additionally, it was noted that a regio-isomer of **2a** was formed in the reaction and the ratio was found to be related to the reaction time. The substrate **1a** could be transformed into a mixture of **2a** and **2a'** in a 5.9:1 ratio with a NMR yield of 84% in 5 min. Prolonging the reaction time leads to a higher ratio of **2a** to **2a'** with a little change of the yield, which suggests that **2a'** could be slowly transformed into **2a** under the reaction conditions.

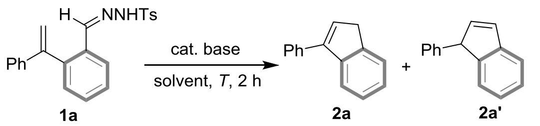
---

[*] Q. Zhou, S. Li, Y. Zhang, Prof. Dr. J. Wang
Beijing National Laboratory of Molecular Sciences (BNLMS) and Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871 (China); Email: wangjb@pku.edu.cn

Prof. Dr. J. Wang
The State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032 (China)

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Table 1: Optimization of the reaction conditions.[a]



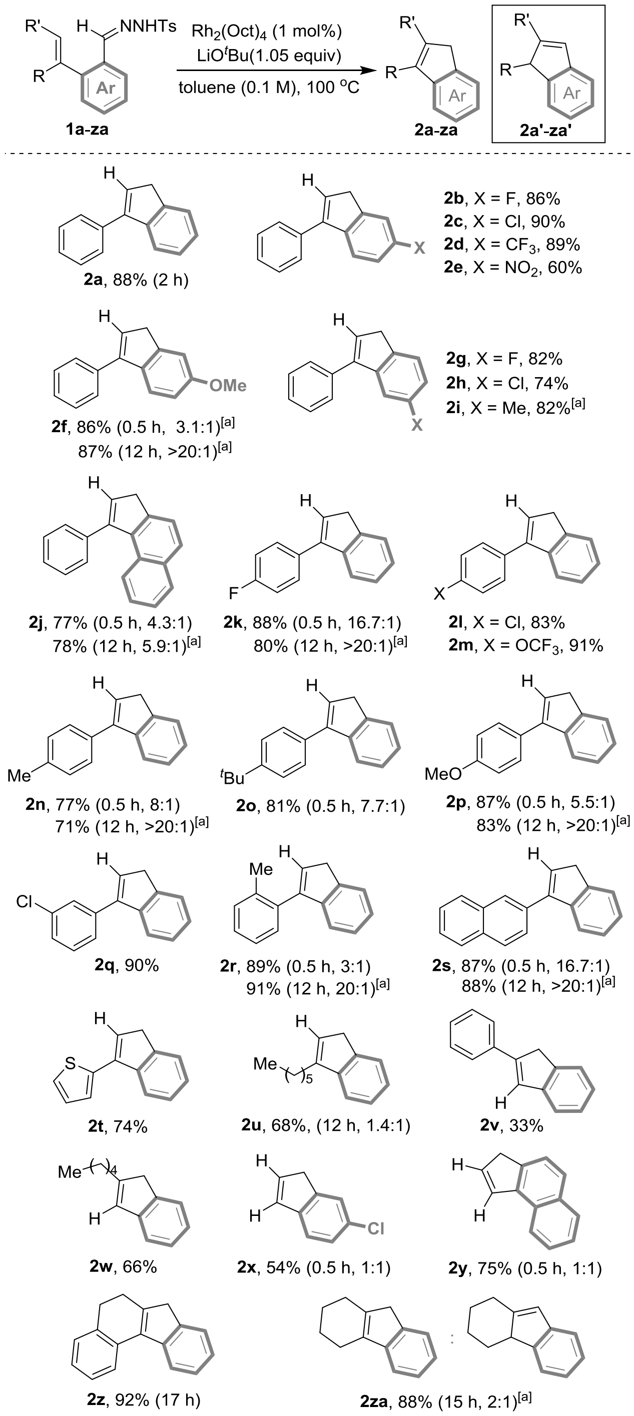
entry	cat.(mol%)	base(eq)	solvent	T (°C)	yield (%)[b]
1[c]	Rh$_2$(OAc)$_4$(1)	LiO^{t}Bu(1.2 eq)	DCE	100	38
2[c]	Rh$_2$(OAc)$_4$(1)	LiO^{t}Bu(1.2 eq)	dioxane	100	74
3[c]	Rh$_2$(OAc)$_4$(1)	LiO^{t}Bu(1.2 eq)	toluene	100	80
4	Rh$_2$(OAc)$_4$(1)	LiO^{t}Bu(1.1 eq)	toluene	70	30
5	Rh$_2$(OAc)$_4$(1)	LiO^{t}Bu(1.1 eq)	toluene	80	49
6	Rh$_2$(OAc)$_4$(1)	LiO^{t}Bu(1.1 eq)	toluene	90	78
7	Rh$_2$(OAc)$_4$(1)	LiO^{t}Bu(1.1 eq)	toluene	110	78
8	Rh$_2$(OAc)$_4$(1)	NaH(1.1 eq)	toluene	100	45
9	Rh$_2$(OAc)$_4$(1)	NaOMe(1.1 eq)	toluene	100	36
10	Rh$_2$(OAc)$_4$(1)	Cs$_2$CO$_3$(1.1 eq)	toluene	100	28
11	Rh$_2$(TFA)$_4$(1)[d]	LiO^{t}Bu(1.05 eq)	toluene	100	24
12	Rh$_2$(Oct)$_4$(1)[e]	LiO^{t}Bu(1.05 eq)	toluene	100	88
13[c]	Cu(OTf)$_2$(5)	LiO^{t}Bu(1.05 eq)	toluene	100	15
14[c]	Pd(OAc)$_2$(5)	LiO^{t}Bu(1.05 eq)	toluene	100	15
15[c]	Co(acac)$_2$(5)	LiO^{t}Bu(1.05 eq)	toluene	100	0
16[c]	CuI(5)	LiO^{t}Bu(1.05 eq)	toluene	100	81
17[c]	AuCl$_3$(5)	LiO^{t}Bu(1.05 eq)	toluene	100	*trace*
18[c]	none	LiO^{t}Bu(1.05 eq)	toluene	100	0

[a] If not otherwise noted, the reaction was carried out with **1a** (0.2 mmol) in toluene (2 mL). [b] The yields refer to the isolated products. [c] The reaction was carried out with **1a** (0.1 mmol) in solvent (1 mL). [d] TFA = CF$_3$CO$_2$. [e] Oct = CH$_3$(CH$_2$)$_6$CO$_2$.

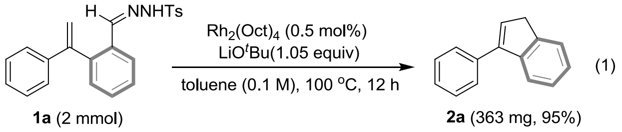
With the optimized reaction conditions in hand, we then started to investigate the substrate scope of the reaction. The substrates with electron-withdrawing groups in the *para*-position of the aromatic ring (Ar) all afforded the corresponding products in good to excellent yields (Scheme 2, **2b**-**e**). When the *para*-position was substituted by a methoxy group, the reaction led to a mixture of **2f** and its isomer **2f'** in 0.5 h, while almost a single product **2f** could be obtained by extending the reaction time to 12 h. The substrates with *meta*-substituents offered the corresponding products in good to excellent yields (Scheme 2, **2g**-**i**). The substrate **1j** produced a mixture of **2j** and **2j'** with the ratio varying from 4.3:1 to 5.9:1, depending on the reaction time (Scheme 2, **2j**).

We then investigated the influence of aromatic substituent of the vinylic double bond (R = Ar). The substrates bearing *para*, *meta*, *ortho*-substituents on the phenyl ring could all afford the corresponding products in good yields (Scheme 2, **2k**-**r**). The substrates bearing naphthyl and thienyl substituent could also give good yields of the corresponding products (Scheme 2, **2s**, **t**). It was noted for some substrates, long reaction time (12 h) was required in order to obtain the products in high isomeric ratio. When the R substituent of the vinylic double bond is a hexyl group, the isomeric products **2u** and **2u'** were formed in a ratio of 1.4:1. In the case where R is H, only single indene product **2w** could be formed. Finally, in the cases where both R and R' are H, the corresponding isomeric indene products were obtained in 1:1 ratio in each case (Scheme 2, **2x**, **2y**). When neither R nor R' is H, the corresponding products were obtained in good yields (Scheme 2, **2z**, **2za**).

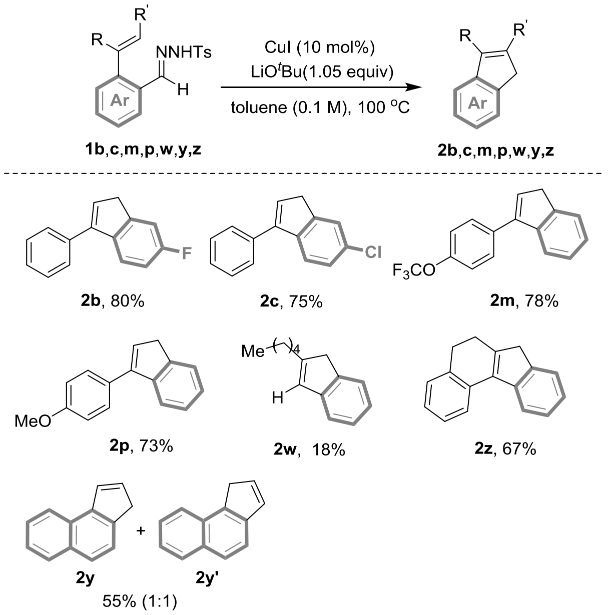
To further demonstrate the practical usefulness of this reaction in synthesis, a scale-up experiment was carried out with 2 mol of the substrate **1a**. In this experiment, the loading of catalyst Rh$_2$(Oct)$_4$ could be reduced to 0.5 mol% and the indene product **2a** could be obtained in 95% yield under identical reaction conditions (eq. 1).



Scheme 2. Reaction scope of the *N*-tosylhydrazones. If not otherwise noted, the reaction conditions are as following: *N*-tosylhydrazone **1a**-**y** (0.2 mmol), Rh$_2$(Oct)$_4$ (1 mol%), LiO^{t}Bu (1.05 equiv), toluene (2 mL), 100 °C, 0.5 h. All the yields refer to the isolated indene products. The numbers in the parentheses refer to the reaction time and the ratio of the isomeric indene products. [a] *N*-tosylhydrazone (0.1 mmol), Rh$_2$(Oct)$_4$ (1 mol%), LiO^{t}Bu (1.05 equiv), toluene (1 mL), 100 °C.



As shown in Table 1 (entry 16), the vinylic C-H bond also occurs smoothly with CuI as the catalyst. Since copper has the advantage of being abundant and cheap, we then investigated the substrate scope of this transformation using CuI as the catalyst. Thus, the CuI-catalysed reaction with a series of substituted *N*-tosylhydrazone substrates could lead to the corresponding indene products in good yields (Scheme 3). However, it was noted that the reaction with the substrate bearing alkyl substituent in the 2-position of the vinylic double bond only afforded a low yield of 18% (Scheme 3, **2w**), while under Rh^{II}-catalyzed condition, the same substrate **1w** afforded the indene product **2w** in 66% yield. It was also noted that the reaction of the *N*-tosylhydrazone bearing no substituent in the vinylic double bond gave the corresponding isomeric indene products **2y** and **2y'** in moderate yield with essentially no selectivity (Scheme 3). The reaction with the substrate which both positions of the vinyl group are substituted afforded a moderate yield (Scheme 3, **2z**).

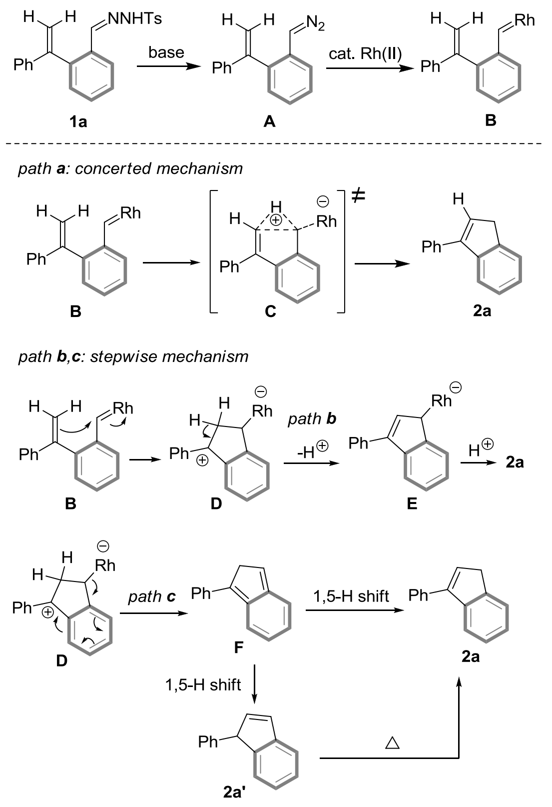


Scheme 3. The scope of the CuI-catalyzed reaction of *N*-tosylhydrazones. If not otherwise noted, the reaction conditions are as following: *N*-tosylhydrazone (0.1 mmol), CuI (10 mol%), LiO^{t}Bu (1.05 equiv), toluene (1 mL), 100 °C, 12 h. All the yields refer to the isolated indene products.

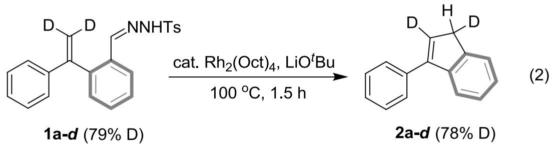
We have proposed three reaction pathways to account for this vinylic C(sp^2)-H bond insertion, as shown in Scheme 4. In the presence of base, diazo intermediate **A** is generated from *N*-tosylhadrazone **1a**, which undergoes dediazoniation to form Rh^{II} carbene **B** intermediate. From Rh^{II} carbene **B** there are three possible pathways. For path ***a***, direct insertion of Rh^{II} carbene **B** into vinylic C-H bond occurs in a concerted manner through transition state **C**. Although Rh^{II} carbene insertion into C(sp^3)-H bond are well established as concerted process,[11] the corresponding concerted insertion into vinylic C(sp^2)-H bond is less likely in view of the fact that the analogous aromatic C(sp^2)-H bond insertion is believed to follow stepwise electrophilic substitution mechanism.[12] Moreover, concerted insertion does not account for the formation of isomeric product **2a'**.

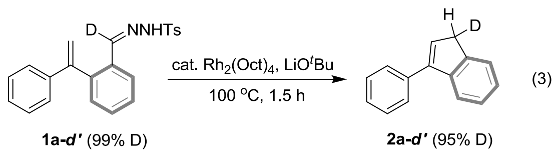
For path ***b*** and ***c***, the nucleophile attack of the vinylic double bond to the electron-deficient carbenic carbon center of Rh^{II} carbene **A** leads to intermediate **D**. In path ***b***, the intermediate **D** releases a proton to form the intermediate **E**, which undergoes protonation to afford product **2a**. However, neither path ***b*** explains the formation of **2a'**. Thus, the plausible pathway is path ***c***, in which the intermediate **D** first undergoes the release of Rh^{II} catalyst to give a dearomatized intermediate **F**. From **F**, 1,5-hygrogen shift can afford both **2a** and **2a'**. Under prolonged reaction at 100 °C, **2a'** isomerizes to thermodynamically more stable **2a**.

To substantiate the proposed reaction mechanism, some mechanistic experiments were carried out. Firstly, deuterium-labelling experiments were conducted with the substrates **1a-*d*** and **1a-*d'*** (eq. 2 and eq. 3). The experimental results showed that deuterium atoms were nearly all retained in the products. Thus, the results do not support path ***b***, where there should be H/D exchange in the deprotonation/protonation process.

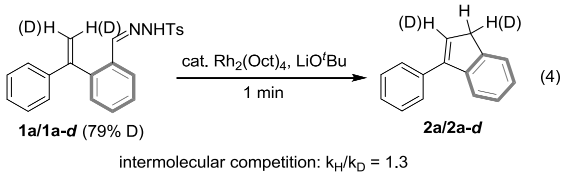


Scheme 4. Proposed reaction pathways.



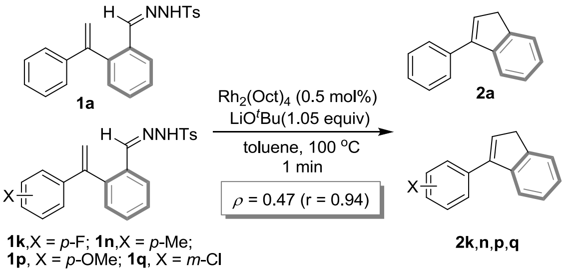


Secondly, the KIE experiments were conducted by using the substrates **1a** and **1a-*d*** (eq. 4). No evident primary KIE was observed in both intermolecular competition experiments and parallel experiments. The results are not supportive to path ***a***, in which concerted C-H bond insertion is expected to show certain level of primary KIE. The lack of primary KIE also suggests that C-H bond cleavage is not involved in the rate-limiting step.[13]



intermolecular competition: $k_H/k_D = 1.3$
parallel experiments: $k_H/k_D = 1.1$

Finally, electronic effects of the reaction was analysed with Hammett linear free energy correlation study (Scheme 5). Moderately good linear correlation could be obtained, giving a reaction constant of ρ = 0.47 (r = 0.94). The relatively small positive reaction constant suggests that for path ***c***, the formation of intermediate **D** is not likely to be the rate-limiting step. Otherwise, a negative reaction constant with large value should be expected, because in this step a positive charge is developed at the carbon adjacent to the substituted aromatic ring. The observed reaction constant suggests that the dearomatization of the intermediate **D** to generate **F** is likely to be the rate-determining step. This is also consistent with the KIE experiments, because C-H bond cleavage is not involved in this step.



Scheme 5. Hammett linear free energy correlation study.

In conclusion, we have developed an efficient method for the synthesis of substituted 1*H*-indenes *via* intramolecular Rh^{II}- or Cu^{I}-catalyzed carbene insertion into vinylic C(sp^2)-H bonds. This work represents a rare example of a formal carbene insertion into a vinylic C(sp^2)-H bonds.[9] The reaction occurs smoothly with high yields and good functional group tolerance, thus providing a straightforward method for the synthesis of 1*H*-indene derivatives.[14] Mechanistic study suggests that this formal vinylic C(sp^2)-H insertion is analogous to the corresponding aromatic C(sp^2)-H bond insertion.

Acknowledgements

The project is supported by National Basic Research Program of China (973 Program, No. 2015CB856600) and NSFC (Grant 21332002).

Conflict of interest

The authors declare no conflict of interest.

Keywords: diazo compounds · insertion reaction· metal carbene · *N*-tosylhydrazone · indene

[1] For selected reviews on carbene C-H bond insertions: a) Taber, D. F. *Formation of C-C Bonds by C-H Insertion.* Houben-Weyl, Methods of Organic Chemistry, V. E21, Helmchen, G. Ed., Georg Thiem Verlag, Stuttgart, 1995; b) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417; c) M. P. Doyle, R. Duffy, M. Ratnikov, *Chem. Rev.* **2010**, *110*, 704; d) H. Lu, X. P. Zhang, *Chem. Soc. Rev.* **2011**, *40*, 1899; e) H. M. L. Davies, D. Morton, *Chem. Soc. Rev.* **2011**, *40*, 1857; f) C.-M. Che, V. K.-Y. Lo, C.-Y. Zhou, J.-S. Huang, *Chem. Soc. Rev.* **2011**, *40*, 1950; g) M. P. Doyle, M. Ratnikov, Y. Liu, *Org. Biomol. Chem.* **2011**, *9*, 4007; h) A. Caballero, P. J. Pérez, *Chem. Soc. Rev.* **2013**, *42*, 8809; i) M. Boultadakis-Arapinis, C. Lescot, L. Micouin, T. Lecourt, *Synlett* **2013**, *24*, 2477; j) J. Egger, E. M. Carreira, *Nat. Prod. Rep.* **2014**, *31*, 449; k) C. Zheng, S. -L. You, *RSC Adv.* **2014**, *4*, 6173; l) B. Wang, D. Qiu, Y. Zhang, J. Wang, *Beilstein J. Org. Chem.* **2016**, *12*, 796.

[2] For recent example, see: K. Liao, S. Negretti, D. G. Musaev, J. Bacsa, H. M. L. Davies, *Nature* **2016**, *533*, 230.

[3] H.-Y. Thu, G. S.-M. Tong, J.-S. Huang, L.-F. S. Chan, Q.-H. Deng, C.-M. Che, *Angew. Chem.* **2008**, *120*, 9893; *Angew. Chem. Int. Ed.* **2008**, *47*, 9747.

[4] A. Caballero, E. Despagnet-Ayoub, M. M. Díaz-Requejo, A. Díaz-Rodríguez, M. E. González-Núñez, R. Mello, B. K. Muñoz, W.-S. Ojo, G. Asensio, M. Etienne, P. J. Pérez, *Science* **2011**, *332*, 835.

[5] For selected recent examples, see: a) W.-W. Chan, S.-H. Chan, Z. Zhou, A. S. C. Chan, W.-Y. Yu, *Org. Lett.* **2010**, *12*, 604; b) E. Rodriguez-Cárdenasand, R. Sabala, M. Romero-Ortega, A. Ortiz, H. F. Olivo, *Org. Lett.* **2012**, *14*, 238; c) Z. Yu, B. Ma, M. Chen, H.-H. W, L. Liu, J. Zhang, *J. Am. Chem. Soc*. **2014**, *136*, 6904; d) C. Zhai, D. Xing, C. Jing, J. Zhou, C. Wang, D. Wang, W. Hu, *Org. Lett.* **2014**, *16*, 2934; e) Z. Liu, H. Tan, L. Wang, T. Fu, Y. Xia, Y. Zhang, J. Wang, *Angew. Chem.* **2015**, *127*, 3099; *Angew. Chem. Int. Ed.* **2015**, *54*, 3056.

[6] a) X. Zhao, G. Wu, Y. Zhang, J. Wang, *J. Am. Chem. Soc.* **2011**, *133*, 3296; b) Z. Liu, J. Wang, *J. Org.Chem.* **2013**, 78, 10024.

[7] F. Hu, Y. Xia, C. Ma, Y. Zhang, J. Wang, *Chem. Commun.* **2015**, *51*, 7986.

[8] a) Z. Shi, D. C. Koester, M. Boultadakis-Arapinis, F. Glorius, *J. Am. Chem. Soc*. **2013**, *135*, 12204. b) D. F. Taber, J. C. Amedio, Jr., R. G. Sherrill, *J. Org. Chem.* **1986**, *51*, 3383.

[9] B. G. Das, A. Chirila, M. Tromp, J. N. H. Reek, B. de Bruin, *J. Am. Chem. Soc.* **2016**, *138*, 8968.

[10] a) J. R. Fulton, V. K. Aggarwal, J. de Vicente, *Eur. J. Org. Chem.* **2005**, 1479; b) D. F. Taber, P. Guo, *J. Org. Chem.* **2008**, *73*, 9479; c) J. Barluenga, C. Valdés, *Angew. Chem.* **2011**, *123*, 7626; *Angew. Chem. Int. Ed.* **2011**, *50*, 7486; d) Z. Shao, H. Zhang, *Chem. Soc. Rev.* **2012**, *41*, 560; e) Q. Xiao, Y. Zhang, J. Wang, *Acc. Chem. Res.* **2013**, *46*, 236; f) Y. Xia, J. Wang, *Chem. Soc. Rev.* **2017**, *46*, 2306.

[11] a) D. F. Taber, K. K. Petty, K. Raman, *J. Am. Chem. Soc.* **1985**, *107*, 196; b) M. P. Doyle, L. J. Westrum, W. N. E. Wolthuis, M. M. See, W. P. Boone, V. Bagheri, M. M. Pearson, *J. Am. Chem. Soc.* **1993**, *115*, 958; c) J. Wang, B. Chen, J. Bao, *J. Org. Chem*. **1998**, *63*, 1853.

[12] For selected examples, see: a) E. C. Taylor, H. M. L. Davies, *Tetrahedron Lett*. **1983**, *24*, 5453; b) D. F. Taber, R. E. Ruckle, *J. Am. Chem. Soc.* **1986**, *108*, 7686; c) K. Nakatani, *Tetrahedron Lett.* **1987**, *28*, 165; d) M. P. Doyle, M. S. Shanklin, H. Q. Pho, S. N. Mahapatro, *J. Org. Chem.* **1988**, *53*, 1017; e) N. Etkin, S. D. Babu, C. J. Fooks, T. Durst, *J. Org. Chem.* **1990**, *55*. 1093; f) A. L. Crombie, J. L. Kane, Jr., K. M. Shea, R. L. Danheiser, *J. Org. Chem.* **2004**, *69*, 8652; g) P. Panne, J. M. Fox, *J. Am. Chem. Soc.* **2007**, *129*, 22; h) C. P. Park, A. Nagle, C. H. Yoon, C. Chen, K. W. Jung, *J. Org. Chem*. **2009**, *74*, 6231; i) W.-W. Chan, S.-H. Chan, Z. Zhou, A. S. C. Chan, W.-Y. Yu, *Org. Lett*. **2010**, *12*, 604; j) E. Rodriguez-Cárdenasand, R. Sabala, M. Romero-Ortega, A. Ortiz, H. F. Olivo, *Org. Lett*. **2012**, *14*, 238; k) Z. Yu, B. Ma, M. Chen, H.-H. W, L. Liu, J. Zhang, *J. Am. Chem. Soc*. **2014**, *136*, 6904; l) C. Zhai, D. Xing, C. Jing, J. Zhou, C. Wang, D. Wang, W. Hu, *Org. Lett*. **2014**, *16*, 2934.

[13] Large KIE is expected for thermal [1,5]-H shift, see: Y. Itou, S. Mori, T. Udagawa, M. Tachikawa, T. Ishimoto, U. Nagashima, *J. Phys. Chem. A* **2007**, *111*, 261.

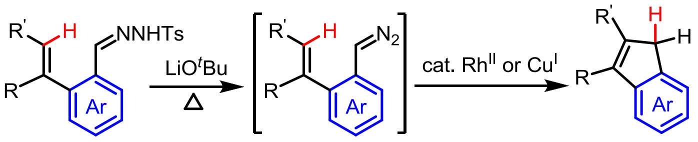
[14] For a recent review of indene synthesis, see: B. Gabriele, R. Mancuso, L. Veltri, *Chem. - Eur. J.* **2016**, *22*, 5056.

Received: ((will be filled in by the editorial staff))

10.1002/anie.201709375

Carbene Coupling

Qi Zhou, Shichao Li, Yan Zhang, Jianbo Wang* _____**Page – Page**



35 examples, up to 92% yield

Formal carbene C(sp^2)-H bond insertion: The Rh^{II}- or Cu^I-catalyzed formal carbene insertion into vinylic C-H bond has been developed. The reaction provides a straightforward method to 1*H*-indenes with high efficiency and good functional group compatibility. The reaction is proposed to follow a stepwise mechanism involving nucleophilic addtion of double bond to metal carbene and dearomatization/aromatization processes.