JOC The Journal of Organic Chemistry

JOCSynopsis

pubs.acs.org/joc

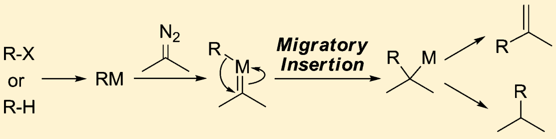
Cross-Coupling Reactions Involving Metal Carbene: From C═C/C−C Bond Formation to C−H Bond Functionalization

Zhenxing Liu[†] and Jianbo Wang*[,†,‡]

[†]Beijing National Laboratory of Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

[‡]State Key Laboratory of Organometallic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

ABSTRACT: Cross-coupling reactions involving metal−carbene are emerging as a new type of carbon−carbon bond-forming reaction. The aim of this JOCSynopsis is to provide an overview of the most recent development of these reactions, focusing on the use of diazo compounds (or in situ formed diazo compounds from *N*-tosylhydrazones) as carbene precursors. In addition, the integration of this type of reaction with C−H bond functionalization is also surveyed.



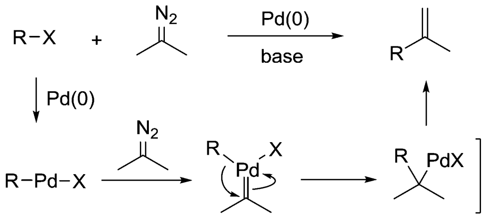
Transition-metal-catalyzed cross-coupling reactions have achieved great success as some of the most important methods for C−C and C−X bond formations.[1] Generally, a cross-coupling reaction consists of an electrophile, a nucleophile, and a transition-metal catalyst. Although many cross-coupling reactions have been established as standard methods in organic synthesis, further studies in this area are still actively underway. Among the various new developments in cross-coupling reactions, the expansion of cross-coupling partners, namely the electrophiles and nucleophiles in the coupling reaction, is particularly attractive. In addition to the traditional halides or pseudo halides (the electrophiles) and organometallic reagents (the nucleophiles), other coupling partners, such as amines and alcohols,[2] carboxylic acids,[3] and esters,[4] have been explored. In recent years, normally inert C−H bonds have been actively explored as coupling partners.[5]

On the other hand, transition-metal-catalyzed transformations through metal−carbene transfer represent another important domain in synthetic methodology.[6] Although transition-metal-catalyzed cross-couplings and metal−carbene transformations have evolved independently over the past decades, studies in the past few years have established the connection between these two fields. A series of novel cross-coupling reactions involving metal−carbene processes has been reported.[7] Mechanistically, these reactions are considered as the integration of classic coupling processes (oxidative addition, transmetalation, reductive elimination, or *β*−H elimination) and metal−carbene processes (carbene formation, migratory insertion). They can also be viewed as the expansion of coupling partners to diazo compounds or tosylhydrazones (the precursors for in situ generation of diazo compounds) for transition-metal-catalyzed cross-coupling reactions. Since this rapidly evolving area has been reviewed very recently,[7] in this JOCSynopsis we will only discuss the latest advances in the field. We will also focus on the recent developments on the integration of this type of reaction with C−H bond functionalization.

C═C DOUBLE BOND FORMATION

As shown in Scheme 1, the key step in the Pd-catalyzed cross-coupling with carbenes is the migratory insertion of the Pd carbene species, which is generated from diazo substrates. A C−C bond and a new C−Pd bond are formed in this process, which is typically followed by *β*-H elimination to afford a C═C bond. Thus, this process constitutes a new method for C═C double bond formation, which is one of the most fundamental transformations in synthetic organic chemistry.

Scheme 1. C═C Double Bond Formation through Pd-Catalyzed Cross-Coupling of Halides and Diazo Compounds



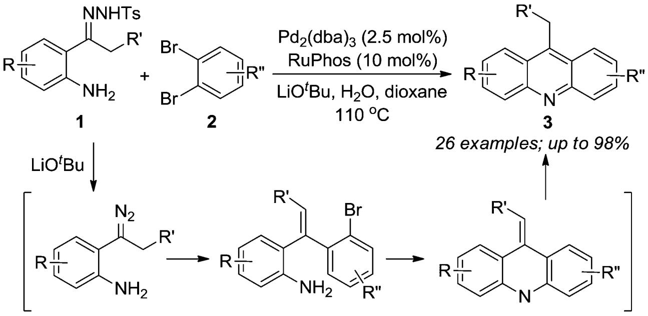
This type of C═C double-bond-forming reaction has been extensively studied in our group and several other groups in the past few years.[7] The area is quickly evolving, and we have seen new advances since the publication of the last review.[7d] One of the interesting new developments is the cascade process or multicomponent process based on this type of C═C double-bond-forming methodology.

As an example of cascade catalytic reaction, we have recently reported a facile and convergent Pd-catalyzed synthesis of acridines **3** using easily accessible *o*-dihalobenzenes **2** and *N*-tosylhydrazones **1** (Scheme 2).[8] The reaction proceeds through two consecutive Pd-catalyzed processes: (1) C═C double bond formation, which is the process depicted in

Received: August 21, 2013
Published: September 13, 2013

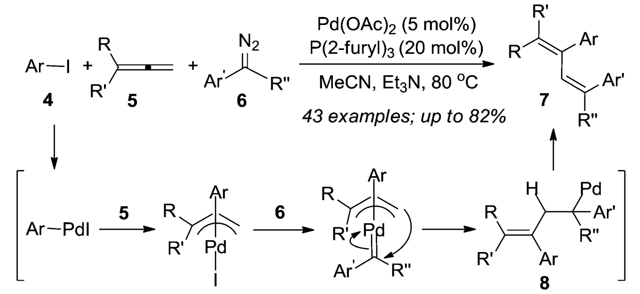
dx.doi.org/10.1021/jo401850q | *J. Org. Chem.* 2013, 78, 10024−10030

Scheme 2. Auto-Tandem Palladium Catalysis: Synthesis of Acridines



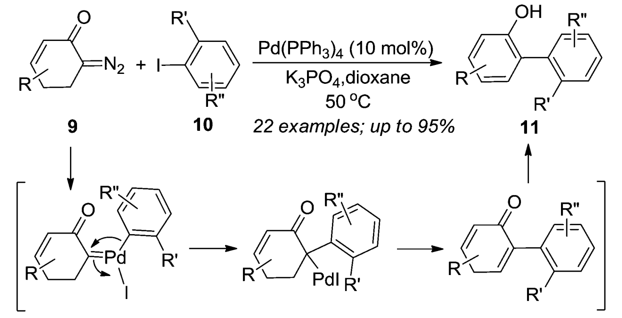
Scheme 1, and (2) C−N cross-coupling (Buchwald−Hartwig coupling). *N*-Tosylhydrazones have long been known as precursors for generating diazo substrates in situ (Bamford−Stevens reaction).[9] This one-pot protocol has wide scope with respect to both coupling partners, providing an efficient access to functionalized acridine derivatives, which are important compounds but in general difficult to synthesize with previous methods. Notably, a single palladium species is employed to catalyze two independent steps in a one-pot fashion, which belongs to a process called autotandem catalysis.[10] Preliminary mechanistic investigation has revealed a favored pathway consisting of fast carbene migratory insertion and β-H elimination sequence, followed by intramolecular C−N cross-coupling.

Scheme 3. Pd-Catalyzed Three-Component Reaction for the Synthesis of 1,3-Dienes



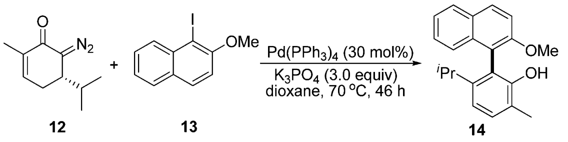
An example of multicomponent reactions involving Pd−carbene is shown in Scheme 3. A Pd-catalyzed three-component coupling of aryl iodides **4**, allenes **5**, and diazo compounds **6** has been reported by our group (Scheme 3).[11] This reaction represents a new direction for 1,3-diene synthesis starting from readily available starting materials. Mechanistically, the reaction involves carbopalladation of the allene and migratory insertion of palladium−carbene. An interesting feature of this three-component coupling is the high stereoselectivity of the newly generated double bonds. The high stereoselectivity for (*E*,*E*)-1,3-dienes **7** formation has been interpreted by the transition state of the *syn* β-H elimination process from palladium intermediate **8**.

Scheme 4. Pd-Catalyzed Synthesis of 2-Arylphenols



The Pd-catalyzed cross-coupling of diazo compounds has also been applied to the synthesis of biaryls through a tandem cross-coupling/aromatization process. Zhai and co-workers have utilized 6-diazo-2-cyclohexenones **9** in Pd-catalyzed cross-coupling with aryl iodides **10** (Scheme 4).[12] Biaryl scaffolds widely exist in ligands, natural products, and pharmaceutical agents. Efficient synthesis of these structures is highly desirable. The new synthesis of 2-arylphenols **11** from aryl iodides **10** and 6-diazo-2-cyclohexenones **9** is efficient and provides a unique method to tackle such problem.

Interestingly, the authors also attempted the application of this reaction to synthesize optically active biaryl compounds from chiral 5-substituted 6-diazo-2-cyclohexenones via point-to-axial chirality transfer. For example, enantioenriched biaryl product **14** was obtained with 72% ee from enantiomerically pure diazo compound **12** (eq 1). Although complete chirality transfer has not yet achieved, the preliminary results do suggest the possibility of synthesizing chiral biaryls through this type of coupling reactions.

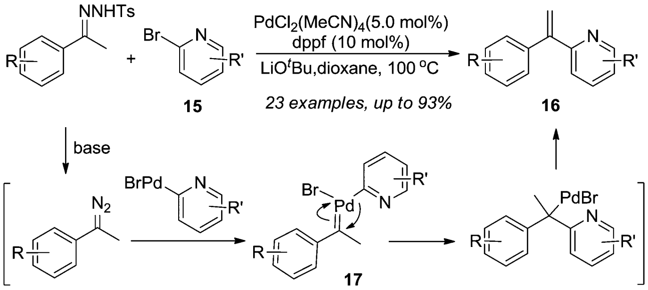


(1)

12 **13** **14**

65% yield, 72% ee

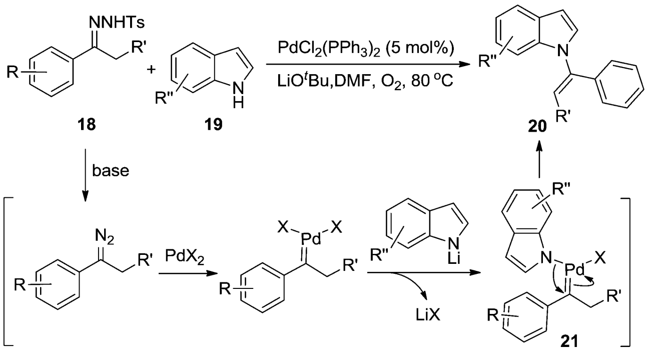
Scheme 5. Pd-Catalyzed Synthesis of 2-α-Styrylpyridines



The aryl halides utilized in Pd-catalyzed coupling with tosylhydrazones have recently been expanded to 2-halopyridines (Scheme 5). Alami and co-workers reported the coupling of *N*-tosylhydrazones with 2-halopyridines **15** to prepare 2-α-styrylpyridines **16**.[13] The reaction involves the migratory insertion of the pyridinyl group in Pd−carbene intermediate **17**. They also evaluated the biological activities of some polyoxygenated derivatives, and some compounds exhibit excellent antiproliferative and antimitotic activities. Recently, the same group has also reported the successful Pd-catalyzed cross-coupling reaction with sterically hindered *N*-tosylhydrazones.[14]

The previous studies have shown that the migratory groups of the Pd−carbene species include aryl, benzyl, vinyl, alkynyl, and cyclopropyl groups.[7d] However, so far the ligand of the palladium−heteroatom bond migratory has not been known. Cui and co-workers have reported the synthesis of *N*-vinylindoles **20** via Pd-catalyzed oxidative coupling of *N*-tosylhydrazones **18** with indoles **19** (Scheme 6).[15a] The reaction is triggered by Pd(II)

Scheme 6. Pd-Catalyzed Synthesis of *N*-Vinylindoles

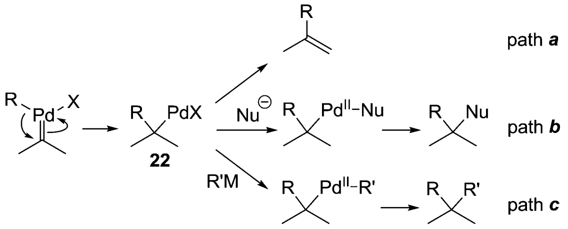


catalyst with O$_2$ as oxidant to complete the catalytic cycle. Notably, the reaction represents the first example of Pd(II)−carbene migratory insertion into Pd−N bond. A similar reaction has been independently reported by Alami and co-workers.[15b]

■ C−C SINGLE BOND FORMATION

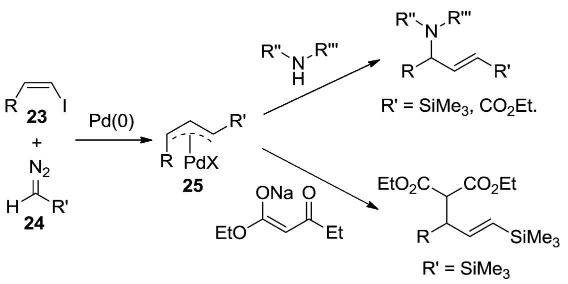
In the Pd-catalyzed C=C bond formation described above, the C−Pd bond generated from the migratory insertion process typically undergoes β-H elimination to afford a C=C bond (Scheme 7, path ***a***). However, the organopalladium intermediate **22** can be trapped by a nucleophile (path ***b***), or it can undergo transmetalation with an organometallic reagent followed by reductive elimination (path ***c***). These transformations further expand the scope of the catalytic reactions based on Pd−carbene. Moreover, these transformations result in the generation of C−C single bond to the carbenic center.

Scheme 7. β-H Elimination versus Other Transformations



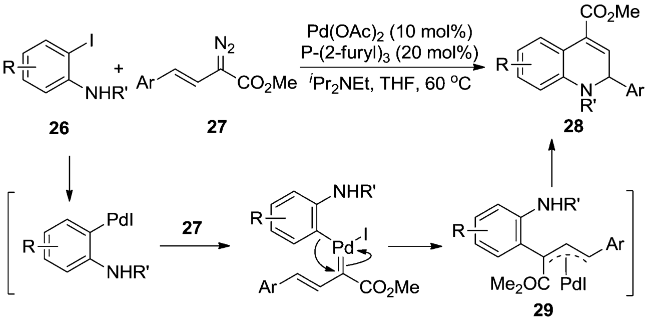
The path ***b*** transformation was mostly explored by Van Vranken and co-workers. They used Pd-catalyzed reactions of allyl halides **23** with diazo compounds **24** to generate allylpalladium species **25**, which could be trapped by amines or enolates (Scheme 8).[16] Recently, the same group reported the use of *N*-tosylhydrazones as carbene precursors in a cascade reaction, in which the generated η^3-allylpalladium species was trapped by an intramolecular amino group. The reaction affords pyrrolidine and piperidine products in good yields.[16d]

Scheme 8. Van Vranken's Pd-Catalyzed Three-Component Coupling Reaction



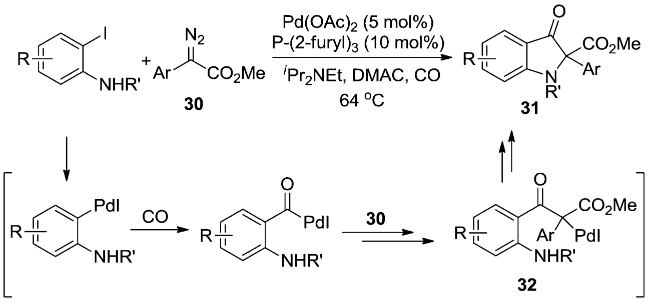
Liang and co-workers reported a Pd-catalyzed synthesis of cyclic amino esters through insertion of α-diazocarbonyl compounds (Scheme 9).[17] Pd-catalyzed reaction of *o*-iodoanilines **26** with arylvinyldiazoacetates **27** affords cyclic α,β-unsaturated γ-amino esters **28**. This reaction explores the nucleophilic attack of the π-allylpalladium species **29** by an internal amino group.

Scheme 9. Pd-Catalyzed Synthesis of Cyclic α,β-Unsaturated γ-Amino Esters



Additionally, aryl diazoacetates **30** lead to cyclic α-amino esters **31** with an α-quaternary carbon center in the presence of CO (Scheme 10).[17] In this case, the nucleophilic attack occurs in palladium species **32**, which is generated by CO insertion/Pd−carbene migratory insertion cascade. Recently, Liang and coworkers expanded this method to Pd-catalyzed insertion of α,β-unsaturated *N*-tosylhydrazones for the synthesis of isoindolines.[18]

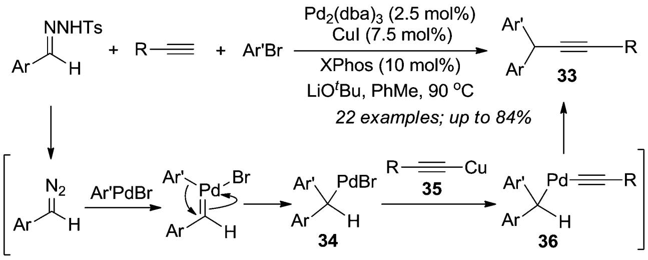
Scheme 10. Pd-Catalyzed CO Insertion/Migratory Insertion Cascade



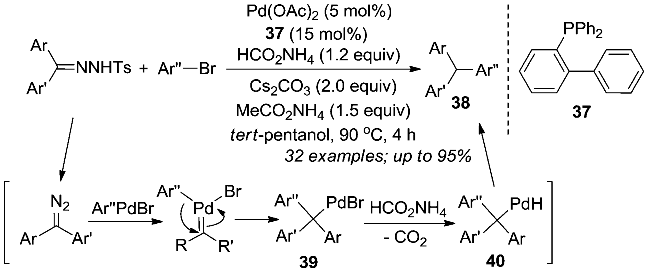
The path ***c*** transformation was first explored by Van Vranken's group in their Pd-catalyzed three-component reaction of trimethylsilyldiazomethane, aryl iodide, and tributylphenyltin, affording benzhydryl derivatives.[19] In 2010, we reported a Pd-catalyzed three-component coupling reaction of *N*-tosylhydrazones, terminal alkynes, and aryl bromides (Scheme 11).[20] In this reaction, the palladium intermediate **34** does not have a β-H. It undergoes transmetalation with the in situ generated alkynyl species **35** to form **36**, which is followed by reductive elimination. Notably, in product **33**, one C(sp^2)−C(sp^3) bond and one C(*sp*)−C(sp^3) bond are formed at the same carbon in a single catalytic reaction.

In the path ***c*** transformation, if R′ is hydride, then the overall transformation is a reductive coupling reaction. We have recently reported a Pd-catalyzed reaction of diarylmethanone *N*-tosylhydrazones with aryl bromides (Scheme 12).[21] In this protocol, the Pd species **39** generated from Pd−carbene

Scheme 11. Pd-Catalyzed Three-Component Coupling Reaction



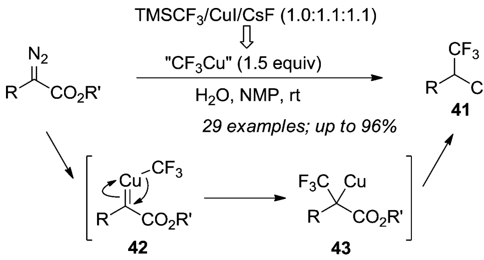
Scheme 12. Palladium-Catalyzed Diarylmethyl C(sp^3)−C(sp^2) Bond Formation



migratory insertion is reduced by HCO_2NH_4 to afford **38** (through **40**). The use of $CH_3CO_2NH_4$ as additive is critical in this reaction since it can significantly suppress the side reaction, namely the direct reduction of the bromide. The ligand also imposes significant effect on the reaction and phosphine ligand **37** provides the optimal results. This reaction represents a new method for the synthesis of triarylmethanes, which have found wide applications in material sciences and medicinal chemistry.

The carbene-based C−C single bond formation strategy has also been utilized for the introduction of a trifluoromethyl group into organic molecules. Hu and co-workers have recently reported a synthesis of α-trifluoromethyl esters **41** by employing a mild Cu-mediated trifluoromethylation of α-diazo esters with $TMSCF_3$ (Scheme 13).[22] This reaction represents the first fluoroalkylation of a nonfluorinated carbene precursor. The reaction mechanism involves the formation of Cu−carbene species **42** from the reaction of diazo substrate with trifluoromethylcopper (CF_3Cu) species. Subsequently, migratory insertion of the carbene ligand into F_3C−Cu bond generates the F_3C−C bond. The authors have suggested that water plays a critical role in activating the "CF_3Cu" intermediate generated from CuI/$TMSCF_3$/CsF.

Scheme 13. Cu-Mediated Trifluoromethylation of α-Diazo Esters

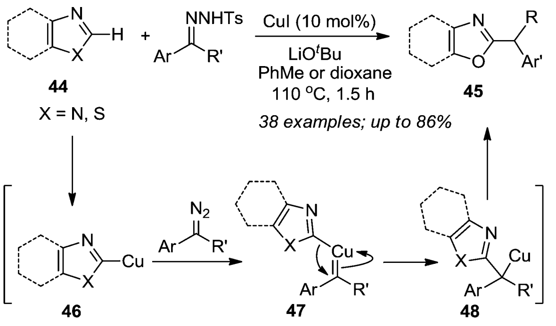


C−H BOND FUNCTIONALIZATION

The reactions described above suggest that the metal−carbene process can be well integrated into the cross-coupling reactions. The key issue of these transformations is the formation of the intermediates containing a C−M bond (M = Pd, Cu, Rh, etc.), which can decompose the diazo compounds to generate metal−carbene species. As has been well-documented in the literature, the C−M bond formation can be achieved through direct C−H bond activations.[5] Therefore, it is conceivable that metal−carbene migratory process can be integrated with transition-metal-catalyzed C−H activation.

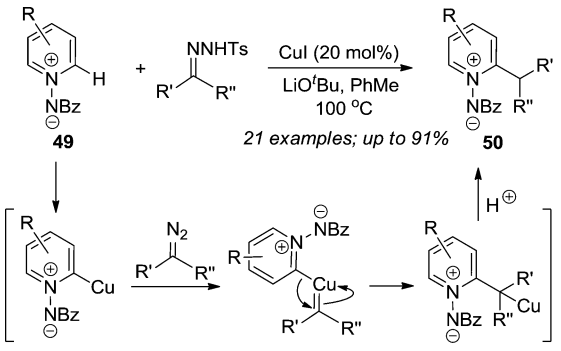
We have demonstrated an example of such process as shown in Scheme 14. This is a Cu-catalyzed direct benzylation or allylation of 1,3-azoles **44** with *N*-tosylhydrazones.[23] The C−H functionalization by secondary benzyl group has been a problem with other transition-metal-catalyzed direct C−H bond functionalization methods. In the reaction mechanism, the key step is the migratory insertion of Cu−carbene species **47**. The Cu species **48** generated from migratory insertion is then protonated to afford the product **45**. An alternative mechanism involving direct Cu−carbene insertion into C−H bond has been removed by experiments. Hirano and Miura late reported direct C−H functionalization of similar 1,3-azoles by using Ni(II) or Co(II) catalysts.[24] In their report, the reaction was extended to more general alkyl-substituted *N*-tosylhydrazones.

Scheme 14. Cu(I)-Catalyzed Direct Benzylation of 1,3-Azoles



Recently, we have reported another similar Cu-catalyzed C−H functionalization of heteroaromatics as shown in Scheme 15. This is a Cu-catalyzed direct alkylation of *N*-iminopyridinium ylides **49** with *N*-tosylhydrazones.[25] In recent years, the development of synthetic methodologies toward substituted pyridine derivatives has attracted significant attentions. This reaction

Scheme 15. Cu-Catalyzed Direct Alkylation of *N*-Iminopyridinium Ylides

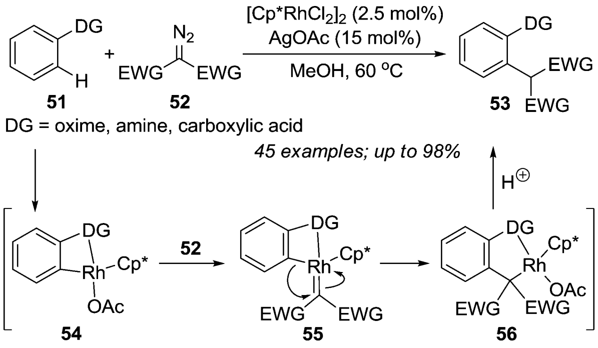


represents an alternative approach toward both primary and secondary *o*-alkyl-substituted pyridine derivatives. The proposed reaction mechanism, which is supported by DFT calculations, is similar to that shown in Scheme 14. The *N*-iminobenzoyl (NBz) moiety functions as directing group to control the regioselectivity through chelation-assisted *ortho*-metalation.

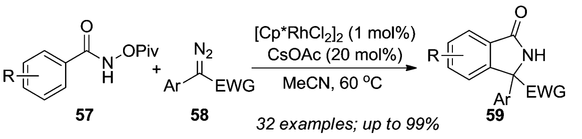
Although palladium complexes have been extensively employed in the study of C−H functionalization, similar integration of C−H functionalization with Pd−carbene migratory insertion so far has not been successful. This may be attributed to the fact that diazo substrates are not compatible with the acidic reaction conditions normally employed in Pd-catalyzed C−H functionlization.[5] On the contrary, Rh complexes have been recently shown as promising catalysts for C−H functionalization with diazo compounds.[26]

In 2012, Yu and co-workers reported Rh(III)-catalyzed intermolecular carbenoid functionalization of aromatic C−H bonds by *α*-diazomalonates **52** (Scheme 16).[27] The reaction is under base-free conditions and uses oxime, carboxylic acid, and amine as directing groups. The reaction mechanism involves the chelation-assisted electrophilic metalation of the *ortho* C(sp^2)−H bond to form rhodacyclic intermediate **54**, followed by Rh−carbene **55** formation, migratory insertion to form **56**, and finally protonation to afford **53**. More recently, Li and co-workers reported similar reactions with other directing groups including pyrazole, pydimidine, and oxazole.[28]

Scheme 16. Rh(III)-Catalyzed C−H Functionalization with *α*-Diazomalonates



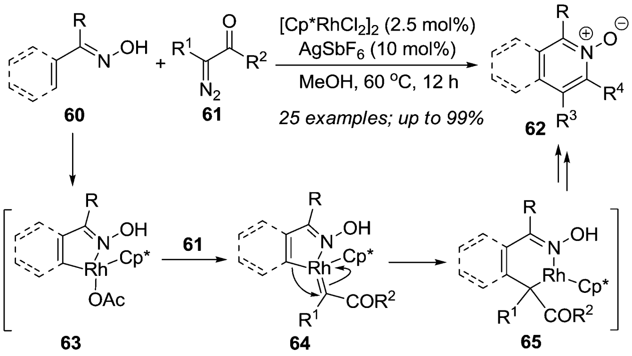
Notably, the Rh(III)-catalyzed reaction discussed above all use the diazo compounds bearing two electron-withdrawing groups. Rovis and co-workers reported Rh(III)-catalyzed coupling of donor/acceptor diazo compounds with *O*-pivaloyl benzhydroxamic acids, providing isoindolones in high yields (eq 2).[29] KIE experiment has suggested that C−H activation is the rate-limiting step. Moreover, intramolecular competition studies show that insertion of the diazo compound favors electron-deficient substrates, which contrasts to the classic Rh(II)−carbene C−H insertions.[6,26] The reaction likely involves a Rh(I)/Rh(III) cycle and the directing group also functions as oxidant.



(2)

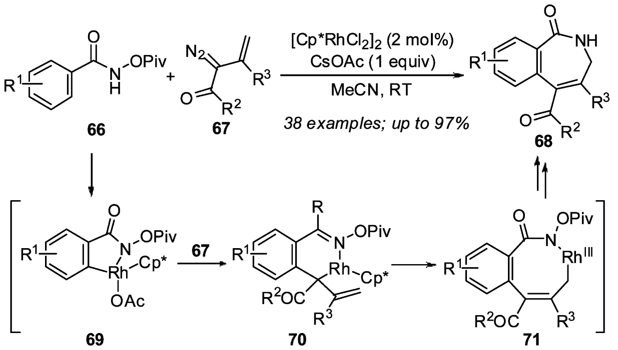
Very recently, Glorius and co-workers disclosed their study on Rh(III)-catalyzed reaction of oximes and diazo compounds (Scheme 17).[30] The reaction affords multisubstituted isoquinoline and pyridine *N*-oxides as products in good yields. The reaction mechanism involves similar directing group-assisted C−H bond activation to form rhodacycle intermediate **63**. Subsequently, **63** reacts with diazo compound **64** to form Rh−carbene, which is followed by migratory insertion to generate **65**. From **65**, protonation, keto−enol tautomerization and cyclization occur to deliver the final product **62**. Notably, this reaction needs no external oxidants and releases N$_2$ and H$_2$O as byproducts. Moreover, this study represents the first example of alkenyl C−H functionalization in Rh−carbene-involved reactions.

Scheme 17. Rh(III)-Catalyzed Synthesis of Isoquinolines and Pyridine *N*-Oxides from Oximes and Diazo Compounds



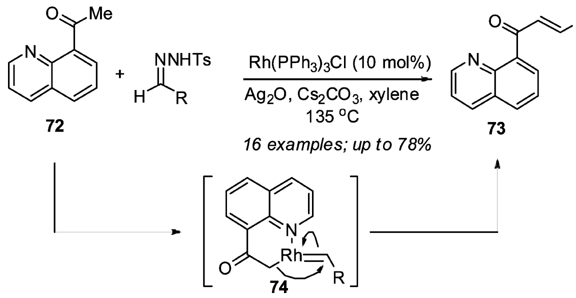
Another Rh(III)-catalyzed C−H functionalization with diazo compounds was recently reported by Cui and co-workers.[31] They use vinyl diazoacetate as carbene precursor. Upon completion of the C−H bond activation/Rh−carbene migratory insertion, the Rh(III) species **70** undergoes 1,3-allylic migratory to generate intermediate **71**, which is finally converted into azepinone product **68** through C−N bond formation/N−O bond cleavage and protonation (Scheme 18). Since 7-membered ring product azepinones are formed exclusively against the possible 5-membered ring products from intermediate **70**, the 1,3-allylic migratory of **70** to **71** must be a rapid process. This work nicely demonstrates the application of vinylcarbenoids as three-carbon components in ring structure construction through C−H bond activation.

Scheme 18. Rh(III)-Catalyzed C−H Activation/[4 + 3] Cycloaddition with Vinylcarbenoids



Compared with C(sp^2)−H functionalization, C(sp^3)−H functionalization is a more challenging problem. Although metal−carbene C−H bond insertion is well-known as a unique way to activate an inert sp^3 C−H bond, this type of reactions is limited by regio- and chemoselectivity.[6] For example, Rh(II)−carbene insertion occurs to electron-rich C−H bonds, and electron-deficient C−H bonds, such as those adjacent to carbonyl groups, usually do not react with Rh(II)−carbene.[32] Wang and co-workers have recently reported a Rh(I)-catalyzed coupling of (quinolin-8-yl)methanone with *N*-tosylhydrazones (Scheme 19).[33] The formal C−H bond insertion occurs at an electron-deficient C−H bond in this case. The proposed key intermediate is Rh−carbene **74**, which undergoes migratory insertion, followed by *β*-H elimination to afford the final products **73**.

Scheme 19. Rh(I)-Catalyzed C(sp^3)−H Functionalization with Tosylhydrazone



CONCLUSION

The transition-metal-catalyzed cross-coupling reaction involving carbene is a rapidly growing area, as can be seen from the publications appeared very recently. These transformations not only enrich the metal−carbene chemistry but also constitute a new type of cross-coupling reaction. It is expected that the combination of metal−carbene migratory insertion with other processes will lead to the further development of novel transformations. Moreover, the metal−carbene migratory process can also be utilized to tackle the problems of C−H bond functionalization, affording some unique solutions to these important issues.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wangjb@pku.edu.cn.

Notes

The authors declare no competing financial interest.

Biographies

Zhenxing Liu obtained his B.S. degree in chemistry from Zhengzhou University in 2011. He is now a third year Ph.D. student in Prof. Jianbo Wang's laboratory at Peking University.

Jianbo Wang obtained his Ph.D. from Hokkaido University in 1990. Upon completion of postdoctoral research at the University of Geneva and University of Wisconsin—Madison, he started his independent research at Peking University in late 1995. He has focused his research on catalytic transformations based on metal−carbenes.

ACKNOWLEDGMENTS

The project is supported by the 973 Program (No. 2009CB825300) and the Natural Science Foundation of China (Nos. 21272010 and 21332002).

REFERENCES

(1) For selected reviews, see: (a) Miyaura, N. *Cross-Coupling Reactions: A Practical Guide*; Springer: Berlin, 2000. (b) Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis: Building Blocks and Fine Chemicals*, 2nd ed.;. Wiley-VCH Verlag: Weinheim, 2004; Vols. *1* and 2. (c) de Meijere, A.; Diederich, F. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; Wiley-VCH Verlag: Weinheim, 2004.

(2) For selected reviews, see: (a) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852−860. (b) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805−818. (c) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046−2067. (d) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131−209.

(3) For recent reviews on decarboxylative coupling, see: (a) Baudoin, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 1373−1375. (b) Gooßen, L. J.; Rodríguez, N.; Gooßen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100−3120. (c) Satoh, T.; Miura, N. *Synthesis* **2010**, 3395−3409. (d) Rodríguez, N.; Gooßen, L. J. *Chem. Soc. Rev.* **2011**, *40*, 5030−5048. (e) Cornella, J.; Larrosa, I. *Synthesis* **2012**, 653−676. (f) Dzik, W. I.; Lange, P. P.; Gooßen, L. J. *Chem. Sci.* **2012**, *3*, 2671−2678.

(4) For reviews, see: (a) Gooßen, L. J.; Gooßen, K.; Stanciu, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 3569−3571. (b) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. *Acc. Chem. Res.* **2010**, *43*, 1486−1495.

(5) For selected reviews on C−H functionalization, see: (a) Chen, X.; Eagle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094−5115. (b) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712−733. (c) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624−655. (d) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147−1169. (e) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215−1292. (f) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315−1345. (g) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740−4761. (h) Arockiam, P. B.; Bruneau, C.; Dixneuf, P. H. *Chem. Rev.* **2012**, *112*, 5879−5918.

(6) For selected reviews, see: (a) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091−1160. (b) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley-Interscience: New York, 1998. (c) Davies, H. M. L.; Manning, J. R. *Nature* **2008**, *451*, 417−424. (d) Zhang, Z.; Wang, J. *Tetrahedron* **2008**, *64*, 6577−6605.

(7) (a) Zhang, Y.; Wang, J. *Eur. J. Org. Chem.* **2011**, 1015−1026. (b) Barluenga, J.; Valdés, C. *Angew. Chem., Int. Ed.* **2011**, *50*, 7486−7500.

(c) Shao, Z.; Zhang, H. *Chem. Soc. Rev.* **2012**, *41*, 560−572. (d) Xiao, Q.; Zhang, Y.; Wang, J. *Acc. Chem. Res.* **2013**, *46*, 236−247.

(8) Huang, Z.; Yang, Y.; Xiao, Q.; Zhang, Y.; Wang, J. *Eur. J. Org. Chem.* **2012**, 6586−6593.

(9) Bamford, W. R.; Stevens, T. S. *J. Chem. Soc.* **1952**, 4735−4740.

(10) (a) Fogg, D. E.; dos Santos, E. N. *Coord. Chem. Rev.* **2004**, *248*, 2365−2379. (b) Wasike, J.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001−1020.

(11) Xiao, Q.; Wang, B.; Tian, L.; Yang, Y.; Ma, J.; Zhang, Y.; Chen, S.; Wang, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 9305−9308.

(12) Yang, K.; Zhang, J.; Li, Y.; Cheng, B.; Zhao, L.; Zhai, H. *Org. Lett.* **2013**, *15*, 808−811.

(13) Lawson, M.; Hamze, A.; Peyrat, J.-F.; Bignon, J.; Dubois, J.; Brion, J.-D.; Alami, M. *Org. Biomol. Chem.* **2013**, *11*, 3664−3673.

(14) Roche, M.; Hamze, A.; Provot, O.; Brion, J.-D.; Alami, M. *J. Org. Chem.* **2013**, *78*, 445−454.

(15) (a) Zeng, X.; Cheng, G.; Shen, J.; Cui, X. *Org. Lett.* **2013**, *15*, 3022−3025. (b) Roche, M.; Frison, G.; Brion, J.-D.; Provot, O.; Hamze, A.; Alami, M. *J. Org. Chem.* **2013**, *78*, 45−454.

(16) (a) Devine, S. K. J.; Van Vranken, D. L. *Org. Lett.* **2007**, *9*, 2047−2049. (b) Kudirka, R.; Van Vranken, D. L. *J. Org. Chem.* **2008**, *73*, 3585−3588. (c) Kudirka, R.; Devine, S. K. J.; Adams, C. S.; Van Vranken, D. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 3677−3680. (d) Khanna, A.; Maung, C.; Johnson, K. R.; Luong, T. T.; Van Vranken, D. L. *Org. Lett.* **2012**, *14*, 3233−3235.

(17) Zhou, P.-X.; Zhou, Z.-Z.; Chen, Z.- S.; Ye, Y.-Y.; Zhao, L.-B.; Yang, Y.-F.; Xia, X.-F.; Luo, J.-Y.; Liang, Y.-M. *Chem. Commun.* **2013**, *49*, 561−563.

(18) Zhou, P.-X.; Luo, J.-Y.; Zhao, L.-B.; Ye, Y.-Y.; Liang, Y.-M. *Chem. Commun.* **2013**, *49*, 3254−3256.

(19) Greenman, K. L.; Carter, D. S.; Van Vranken, D. L. *Tetrahedron* **2001**, *57*, 5219−5225.

(20) Zhou, L.; Ye, F.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2010**, *132*, 13590−13591.

(21) Xia, Y.; Hu, F.; Liu, Z.; Qu, P.; Ge, R.; Ma, C.; Zhang, Y.; Wang, J. *Org. Lett.* **2013**, *15*, 1784−1787.

(22) Hu, M.; Ni, C.; Hu, J. *J. Am. Chem. Soc.* **2012**, *134*, 15257−15260.

(23) Zhao, X.; Wu, G.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 3296−3299.

(24) Yao, T.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 775−779.

(25) Xiao, Q.; Ling, L.; Ye, F.; Tan, R.; Tian, L.; Zhang, Y.; Li, Y.; Wang, J. *J. Org. Chem.* **2013**, *78*, 3879−3885.

(26) Rh(II) complexes have been extensively used as catalysts in carbene C−H bond insertions (see ref 6). These reactions are through direct concerted C−H bond insertion, mostly into the C(sp^3)−H bond. They are different from the Rh-catalyzed reaction described in this paper.

(27) Chan, W.-W.; Lo, S.-F.; Zhou, Z.; Yu, W.-Y. *J. Am. Chem. Soc.* **2012**, *134*, 13565−13568.

(28) Yu, X.; Yu, S.; Xiao, J.; Wan, B.; Li, X. *J. Org. Chem.* **2013**, *78*, 5444−5452.

(29) Hyster, T. K.; Ruhl, K. E.; Rovis, T. *J. Am. Chem. Soc.* **2013**, *135*, 5364−5367.

(30) Shi, Z.; Koester, D. C.; Boultadakis-Arapinis, M.; Glorius, F. *J. Am. Chem. Soc.* **2013**, *135*, 12204−12207.

(31) Cui, S.; Zhang, Y.; Wang, D.; Wu, Q. *Chem. Sci.* **2013**, 3912−3916.

(32) Padwa, A.; Austin, D. J. *Angew. Chem., Int. Ed.* **1994**, *33*, 1797−1815.

(33) Zhang, Y.; Wang, J.; Wang, J. *Synlett* **2013**, 1643−1648.