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Recent Advances of Rhodium Catalyzed Coupling Reactions

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Abstract: **Rh-catalyzed few recent reactions including C–H activation (*sp2* and *sp3*), carbene insertion and boronic acid activations are reviewed. These strategies mostly assist to the development of a widely applicable and efficient protocol to the formation of various C-C (C*sp2*-C*sp2* and C*sp3*-C*sp2*) and C-X bonds in their particular domain; in addition, these new bonds perhaps incorporate important tandem cyclization to produce valuable heterocycles. These reactions highlight the innate nature of rhodium in selectivity as well as reactivity in the C-H bond functionalizations through the generation of organo-rhodium reactive intermediates.**

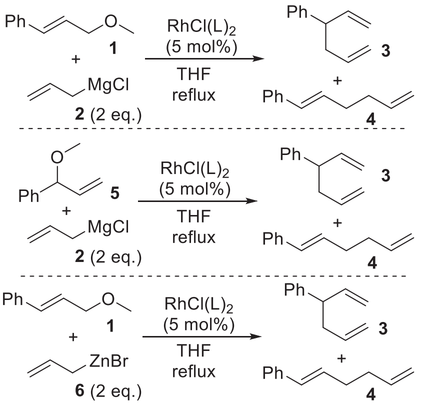
Index Terms: Rh-Catalysis, C-H activation, Carbene insertion, Heterocycles, C-X bonds, MCR

I. INTRODUCTION

Transition metal catalyzed cross-coupling reactions have been well familiar and are being essential tools in modern organic synthesis. Amongst, rhodium complexes are peculiar and most important for organic synthesis due to their ability to catalyze a variety of useful transformations [1-9]. The organic synthesis through rhodium catalysis associates the most recent progress and developments including in the field of cyclization reactions, C-H arylation reactions of arenes/ heteroarenes, multi component reactions and carbene coupling reactions by using rhodium(I) and rhodium(III) complexes [10-12]. In particular, carbene coupling reactions through trans-metalation & C-C activations catalyzed by rhodium(I) catalysts [3-9], additionally, C-H activation centered carbene coupling reactions are catalyzed by rhodium(III) catalysts [10-12]. Apart from its functionality, Rh(I) complexes are efficiently employed for C-X bond formations [13-16], especially in the challenging area bond formations, viz., C-S [17,18], C-Se [18], C-Si [19], and C-P [20] formations. On the other hand, rhodium (II) complexes are very prominent to catalyze C-H bond activations & insertions [21], classical carbene cross coupling reactions, cyclopropanations [22,23], and ylide formations [24]. Generally coupling reactions need a nucleophile and an electrophile as the coupling partners. The transition metal can connect both the fragments of the nucleophile as well as electrophile. Researchers worldwide focus on developing coupling reactions through expanding the new coupling partners.

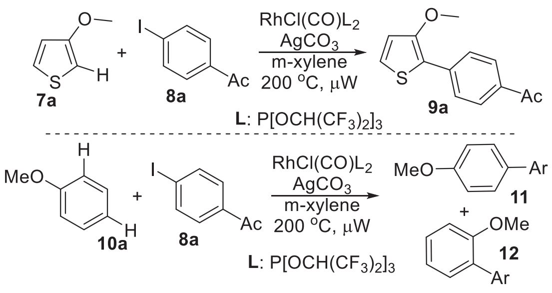
II. RHODIUM CATALYZED COUPLING REACTIONS

Allylation of allylic ethers **1**/**5** with allyl magnesium chloride **2** was carried out by RhCl(L)$_2$ (L may be, nbd- norbornanediene, cod- 1,5-cycloocatdiene) in THF solvent under refluxing conditions to produce corresponding dienes **3** & **4**, and the product ratio depends on the conditions of the reaction and the nature of catalyst (Scheme 1). Apart from Grignard based reagent, RhCl(cod)$_2$ produces similar products of dienes with allylic zinc chloride substrate **6**, wherein the reaction was found to be facilitated by the presence of TMEDA ligand [25].



Scheme 1. Allylation of allyl ethers by Rh (I) complexes

In 2006, Kenichiro Itami and group developed a rhodium complex contains strongly π-acceptor ligands and also found its utility in the C-H arylations of hetero arenes with aryl iodides **8a** (Scheme 2) [26]. This Rh complex is very stable for long time; no decomposition of the material was detected even after 8 months. X-ray studies of this complex revealed that this might have happened as rhodium perhaps completely covered with two bulky ligands, viz., P[OCH(CF$_3$)$_2$]$_3$. In addition, this method also applied for the direct arylation of benzene, but with low efficacy and produces mixture of regio isomers.



Scheme 2. Arylation of arenes/ heteroarens

Rhodium catalysts are also useful for multi component reactions (MCRs), Hayashi et. al. developed rhodium catalyzed MCR that involves cross coupling of organic halides. Reaction of alkyne tethered iodoarene **13** with organic zinc halide **6** in the presence of rhodium catalyst

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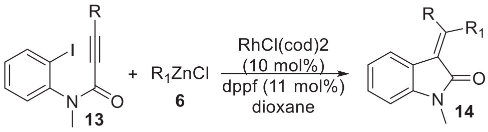
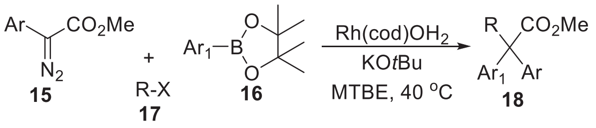
$RhCl(cod)_2$ in dioxane at 40 °C produces the cyclic compound **14** through carborhodation, oxidative addition and followed by reductive elimination. It was mechanistically proved that, this rhodium catalytic cycle is different to palladium catalyzed reaction of Pd(0)/Pd(II) catalytic cycle (Scheme 3) [27].



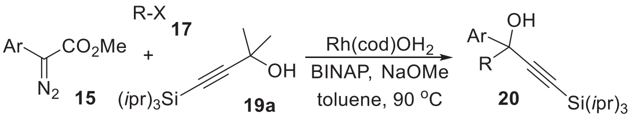
Scheme 3. Rhodium catalyzed arylation followed by cyclization.

In another multi component reaction, it involves rhodium(I) complex [of 1,5-Cyclooctadiene (cod) ligand] catalyzed the cross-coupling reaction of α-aryldizaoacetates **15** with different boronic acids **16** and alkyl halides **17** in the presence of a base KO*t*Bu to generate α,α-heterodiaryl carboxylic esters **18** (Scheme 4) [28]. Initially boronic acid forms organo-rhodium with rhodium complex and it produces allyl complex with diazo compound which finally undergoes alkylation with alkyl halide with the assistance of base to produce α,α-heterodiaryl carboxylic esters.



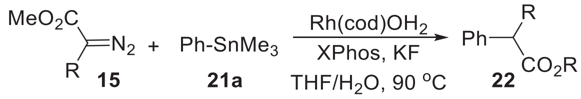
Scheme 4. Rhodium catalyzed cross coupling reaction of diazocarboxylate with boronic acid

Wang, J., et. al. developed a multi component reaction of tertiary propargyl alcohol **19a**, diazo ester **15** and alkyl halide **17** and that was catalyzed by $Rh(cod)OH_2$ with BINAP ligand in the presence of a base NaOMe in toluene solvent produces the product **20** through simultaneous alkyl and alkynyl coupling reactions (Scheme 5) [29]. These two coupling partners are linked with carbene moiety leads to produce C(*sp*)-C(*sp3*) and C(*sp3*)-C(*sp3*) chemical bonds. These reactions are helpful to construct quaternary centers with readily available materials.



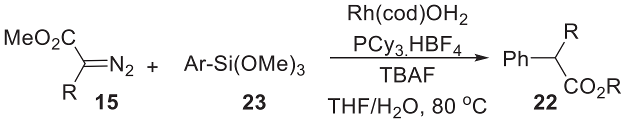
Scheme 5. Rhodium catalyzed successive C(sp)-C(sp3) and C(sp3)-C(sp3) bond formations

In addition, carbene mediated coupling of diazoester **15** with arylstannane **21a** was being developed by the same Wang, J., group (Scheme 6) [30]. The reaction is carried out between diazoester and arylstannane with the aid of the same catalyst $Rh(cod)OH_2$ (2 mol%) and ligand XPhos (10 mol%) in the presence of an additive KF (1 equiv) and in THF/H_2O solvent mixture at 70 °C leads to generate Stille like coupling product **22**. The process of this reaction is very easy and mild and this reaction offers a good method for the synthesis of α-aryl esters molecules.



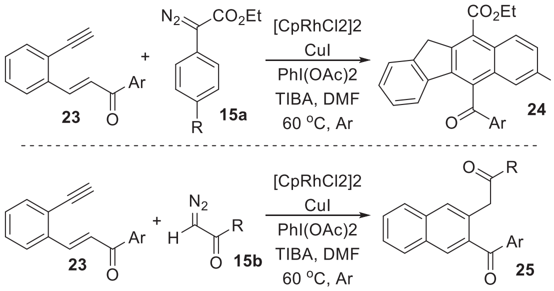
Scheme 6. Rhodium catalyzed Stille type coupling reaction

They also found the utility of diazoesters **15** in the reaction with arylsiloxane reagents **23** in presence of 2 mol% $Rh(cod)OH_2$, 10 mol% of $PCy_3.HBF_4$ and 1 equiv TBAF (Scheme 7) [31]. It is also another example for Csp3-Csp2 coupling reaction and produces the same compound/ α-aryl esters **22**. This reaction was the initial example for arylsiloxanes as coupling agents. This reaction is proceeded through the Rh(I) carbene migratory insertion.



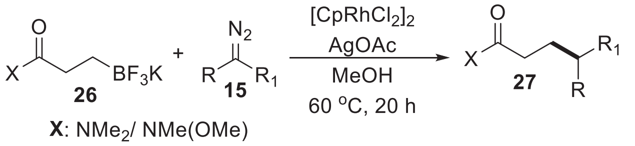
Scheme 7. Rhodium catalyzed diazoester coupling reaction with arylsiloxane

Jiang and his coworkers developed a method to the synthesis of densely functionalized benzo[b]flourenes and 2-napthalenylmethanones through a synergistic bimetallic catalytic pathway, which involves 1.5 mol% $(RhCp^*Cl_2)_2$ and 10 mol% CuI from the reaction of 1,5-eneyn **23** with aryl diazoacetate **15** in the presence of 4 equiv additive TIBN (triisobutylamine) in DMF solvent at 60 °C (Scheme 8) [32]. Amongst, the former reaction happened with aryl diazoester **15a** produces functionalized benzo[b]flourenes **24**; while the second reaction involves the use of ethyl diazoacetate **15b** to generate functionalized napthalenes **25**. The reaction was proved to start with in-situ formed rhodium carbenoids.



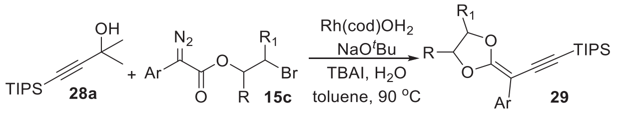
Scheme 8. Rhodium catalyzed synthesis to benzo[b]flourenes and 2-napthalenylmethanones

A coupling reaction of alkyltrifluoroborate **26** with α-diazomalonates **15** was being developed by Yu, W. -Y., and his group through the C(*sp3*)-C(*sp3*) coupling and these coupled products **27** were formed up to 97% yields and it was shown in Scheme 9 [33]. Cp*Rh(III) catalyst along with an additive AgOAc were used for the reaction in methanol solvent. For the diazo partners, useful functional groups, including ketone, ester, amide, ether, sulfonyl, and thiophenes were tested successfully. Mass spectrometry (ESI-MS) study of the reaction clearly indicated that the formation of a distinct molecular species corresponding to σ-alkylrhodium(III) complexes. The successful diazo coupling reaction may be attributed to the coordination of the amide group and that promotes stability of the alkylrhodium (III) complex through the formation of a five membered metallacycle.



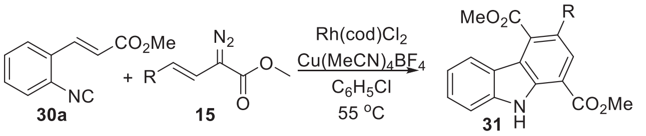
Scheme 9. Rh(III)-catalyzed cross coupling of alkyl trifluoroborate with α-diazomalonates

In one more diazoacetate reaction, cross coupling was observed through rhodium catalyzed reaction between 2-bromoethyl aryldiazoacetates **15c** with tertiary propargyl alcohol **28a** (Scheme 10) [34]. This cross coupling occurred with the assistance of 2 mol% $Rh(cod)OH_2$ catalyst and 1 equiv of NaO*t*Bu, 10 mol% of TBAI phase transfer catalyst in mixture of solvent (water and toluene) to afford carbene involved lactonization to produce **29**. It proceeds through a sequential cleavage of C-C bonds followed by the formation of C(sp2)-C(sp) and C-O bonds.



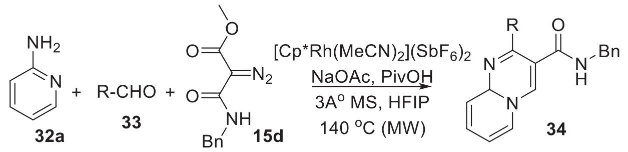
Scheme 10. Rh(III)-catalyzed cross coupling of tertiary propargyl alcohol with diazoacetates

Zhao, Y. L. and his workers reported coupling of diazoacetate followed by cyclization in presence of rhodium catalyst (Scheme 11) [35]. This cyclization occurred between alkenyldiazoacetates **15** with o-alkenyl arylisocyanides **15** with 3 mol% $[Rh(cod)Cl_2]$ and 0.3 equiv of $Cu(MeCN)_4BF_4$ in chlorobenzene at 55 °C for 16 h to produce carbazoles **31**. During this reaction, intramolecular [4+2] cycloaddition/ oxidative aromatization process leads to produce carbazoles.



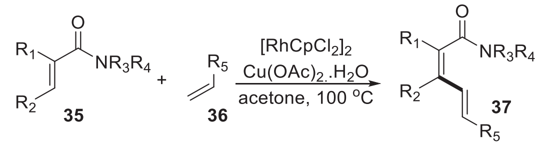
Scheme 11. Rh(III)-catalyzed synthesis to carbazoles

Ellmann, J. A., and coworkers reported a Rh(III) catalyzed multicomponent coupling reaction between aldehydes **32a**, 2-aminopyridines **33** and diazoesters **15d** to produce pyrido[1,2-a]pyrimidine-4-ones **34** (Scheme 12) [36]. This reaction proceeds through imine formation between 2-aminopyridine and aldehyde, and followed by imine C-H activation by Rh(III), carbene insertion and cyclization to generate the final product **34**. The reaction is very comfort with aromatic aldehydes and enolizable aldehydes; in addition, trimethyl orthoformate and DMF dimethyl acetals are also used for the substitute of aldehyde to launch –OMe and dimethylamino functional groups on pyrimidine ring.



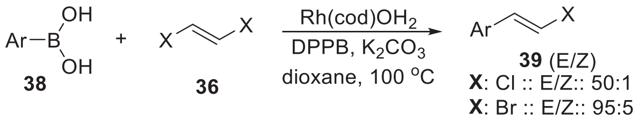
Scheme 12. Rh(III)-catalyzed synthesis to pyrido[1,2-a]pyrimidine-4-ones

Tech-Peng Loh and co-workers developed a rhodium catalyzed direct oxidative cross coupling of acrylamides **35** with olefins **36** to produce (Z,E) dienamides **37**, wherein they used a co-oxidant $Cu(OAc)_2.H_2O$ along with rhodium complex $[RhCl_2Cp^*]_2$. This reaction indicates the rhodium complex ability in the generation of Csp2- Csp2 cross coupling reaction, and it had shown a wide substrate flexibility and functional group compatibility (Scheme 13) [37].



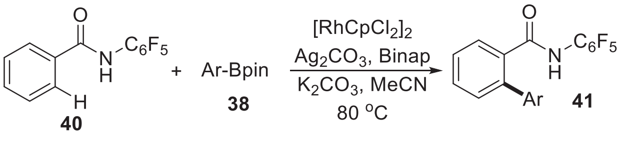
Scheme 13. Rhodium catalyzed sp2-sp2 cross coupling reaction

A similar sort of coupling was achieved by Miura and group in a reaction between aryl boronic acids **38** and alkenyl dihalides **36** and that was catalyzed by 3 mol% of $Rh(cod)OH_2$ and 6 mol% of 1,4-bis(diphenylophosphino)butane (DPPB) in presence of K_3PO_4 in dioxane solvent and refluxed at 100 °C for about 8 to 15 h produces mono-arylated olefins **39** (Scheme 14) [38]. This reaction is worked well with 1,2-dichloro and 1,2-dibromo alkenes, and yielded products in appreciable yields with regioselectivity wherein it produces E-isomer majorly rather Z-isomer. Moreover, the reaction of 1,1-dihalo alkene under the said conditions produces corresponding di-arylated product with aryl boronic acids but with less yield.



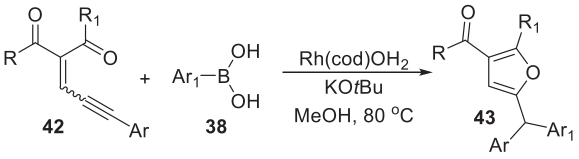
Scheme 14. Rhodium catalyzed mono-arylation of alkenylhalides with aryl boronic acids

Yu and his group developed a rhodium catalyzed C-H arylation of arenes with phenyl boronic acid esters **38** (Scheme 15). In this reaction, the ability of $[Cp^*RhCl_2]_2$ catalyzed reaction was considerably increased by bidentate phosphine ligand (BINAP). The reaction is initiated by the presence of an easily labile donating group N-pentafluorophenylbenzamide **40** for the first time as an auxiliary. The reaction offers a practical and general method to this C-H arylation of versatile benzamide and boronic ester substrates [39].



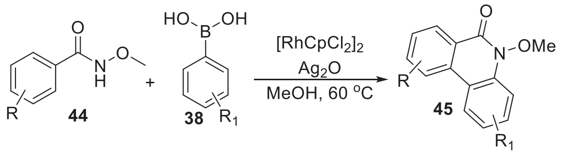
Scheme 15. Rhodium catalyzed C-H arylation

Apart from diazo compounds as carbene precursors, Wang and coworkers are being used conjugated enynones **42** as a carbene precursor with boronic acids **38** in the synthesis of furyl containing triarylmethanes **43** through a rhodium catalyzed method (Scheme 16) [40], wherein 2 mol% of Rh(cod)(OH)$_2$ and 1 equiv of base KOtBu were used in MeOH solvent at 80 ^oC. These mild reaction conditions are facilitated to the synthesis of functionalized furan compounds. The reaction involves Rh(I) carbene formation, migration, insertion in a sequence in the generation of products.



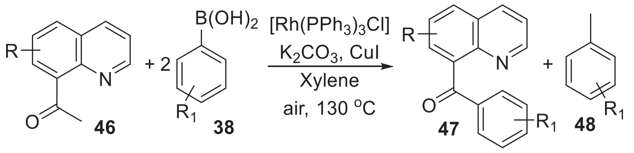
Scheme 16. Rhodium catalyzed synthesis to furan compounds

Regioselective synthesis of phenanthridinone heterocycles **45** were achieved from N-methoxy benzamides **44** and aryl boronicacids **38** through the Rh(III) catalysis (Scheme 17). It involves one pot C-C/C-N bond formation leads to a (4+2) cyclization in a milder approach. This transformation was initiated by Ag$^+$ through the removal of halide ion from the catalyst in presence of ligand, during process Rh(III) converted to Rh(I) and which is re-oxidized to the required catalyst by the oxidation of Ag2O to further catalytic action [41].



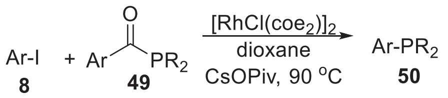
Scheme 17. Rhodium (III) catalyzed synthesis of phenanthridinones

Along with regular C-H activations/ functionalizations, rhodium could produce C-C activation and utilization of this protocol into a new bond formation with boronic acids. Wang, J., and coworkers discovered rhodium catalyzed direct exchange of the methyl/ aryl group of a ketone with another aryl group from boronicacid (Scheme 18) [42]. In this reaction 1-(quinolin-8-yl)ethanone substrates **46** were treated with boronicacids **38** in the presence of Rh(PPh$_3$)Cl, CuI, and a base K$_2$CO$_3$ refluxed at 130 ^oC in xylene. The reaction was initiated directly with C-C activation through Rh(I) complex formation and subsequent boronicacid transmetalations by Rh(I)/Rh(III) catalytic cycle produces the coupling product **48**.



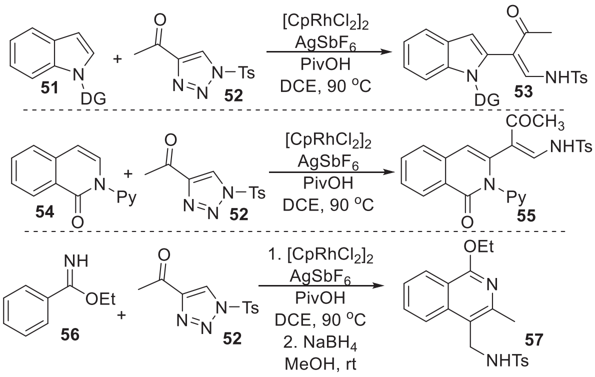
Scheme 18. Rhodium (I) catalyzed C-C activation with boronicacids

Wang, Z., and his group developed the rhodium catalyzed C-P cross coupling reaction by the reaction of aryl iodides **8** with acylphosphines **49** which served as reagent as well as ligand in this reaction. Generally, these C-P cross coupling reactions are familiar with transition element catalysis, but Rh(I) catalyzed C-P formations are rare. This reaction was the foremost example for rhodium catalyzed C-P bond formation (Scheme 17) [20].



Scheme 19. Rh(I) catalyzed C-P cross coupling reaction

Li, X., and his coworkers were being used 4-acyl-1-sulfonyltriazoles **52** as carbene source in Cp*Rh(III) catalyzed C-H bond activation of ortho-selective coupling reaction and described in Scheme 18. This coupling reaction produces olefin and later with further feasibility, undergoes cyclization to generate cyclized product **57** (on the basis of nature of arene) [43].



Scheme 20. Rh(III) catalyzed C-C coupling of arenes with sulfonyltriazoles

III. CONCLUSIONS

In summary, we present the recent reaction profile and scope of the rhodium catalyzed coupling reactions that are important in the synthetic organic chemistry as its selective reactivity and carbene insertion reactions by its feasible organometallic intermediate formation. Particularly, these mild approaches afford a wide range of powerful, general and efficient methods for the construction of intricate aza-fused heterocycles, polycyclic structures and heterocyclic scaffolds. However, the noteworthy achievements have been made, still challenging rhodium catalyzed reactions associates multiple C-H bond activations, direct C-H bond activation without the involvement of metal chelation and innate *sp3*C-H activations remains offer a great scope to chemists worldwide. Eventually, these rhodium catalyzed reactions are to be a tool in future to construct various stimulating organic structural frameworks.

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