

## REVIEW ON CATALYTIC CH INSERTION AND FUNCTIONALIZATION OF ORGANIC COMPOUNDS

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In this review, numerous chemical reactions of CH insertion have been presented. The insertion and reactivity of CH bond has been enhanced by the using of different types of catalytic coordination compounds. The inserted CH bond has been utilized in the synthesis of different types of important and useful organic compounds. The main break through was found by using the transition elements as catalysts for the CH insertion, reactivity and conversion.

**Keywords:** CH Insertion, Reactivity, Catalysts and Transition Elements.

**INTRODUCTION**

The activation of a molecule or organic compound refers to the increase its reactivity due to carrying out some structural changes i.e CH insertion [1]. It is reasonable to explain that activated C-H bond can increase reactivity or excitation energy of an organic compound toward a chemical reagent. The present work of CH insertion in Organ metallic Chemistry is devoted to recent advances in metal complexes, inert and unreactive chemical bonds. The synthetic utility of inserting C-H bonds in different types of organic compounds becoming now the point of attention. Specifically, *orthometallation* of aryl groups attached to coordinated donor atoms was among the first examples of direct C-H bond insertion in a transition metal complex. This work demonstrated that an M-C (aryl) fragment and a metal hydride could be formed directly by oxidative addition of an *ortho* H-C (aryl) group [2-8]. However, the manufacture of aryl halides is not an environmentally friendly process and thus the future of bulk aromatic synthesis may lie in the direct insertion of C-H bonds. For example, the formation of benzaldehyde from the insertion of CO into a C-H bond of benzene is a recent development in this area [9].

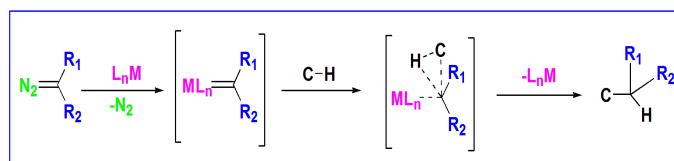
**Literature review**

The first homogeneous catalysis of C-H insertion and functionalization reactions by transition metal complexes was carried out by Fenton in 1894 [10]. However, the modern development in the CH activation and insertion was named as Shilov's platinum chemistry from 1970 [11] and Labinger has contributed a lot in the form of his reviews [12]. A variety of metals and mechanisms have be reviewed by *Weiping Su et al* on decarboxylative C-H functionalization [13]. The catalytic enantioselective transformations were quoted by Cramer and co-workers also rely heavily on Pd [14]. *Ellman et al* reviewed a wide variety of metals, both precious and base, for catalyzed C-H bond addition to polar groups [15]. A wide variety of metals catalyze acceptorless dehydrogenative alcohol oxidation, as presented by *Crabtree et al* [16] who also includes applications to heterocycle synthesis and hydrogen storage.

*Chang et al* presented catalyzed C-H involving a variety of metals [17]. C-H functionalization of azines was reviewed by *Murakami et al* [18]. *Guangbin Dong et al* came across at CH alkylation with alkenes as the alkylating agent [19]. C-C activation has also gained attention, with the main reactivity being shown by strained ring systems, as represented by *Bower et al* [20]. *Qin et al* reviewed a variety of useful CH functionalizations [21]. So, C-H insertion and functionalization now provides a potential way to simplify synthetic strategies as well as permit a wider variety of final products to be made from the same late stage intermediate in realty. The past twenty years have seen a substantial shift of focus and thinking in the field of C-H bond insertion and functionalization at metal centres. Although much remains to be learned about the processes and factors controlling the activity and selectivity of catalytic alkane activation, insertion and functionalization. The main difficulty ahead now lies with using and increasing this knowledge in order to develop practical processes that exploit alkane transformation chemistry.

**CH Insertion**

The process in which a formal insertion of a carbene CR<sub>1</sub>R<sub>2</sub> group into a C-H bond which is accomplished with the help of metal-based catalysts and diazo reagents [22]. These transformations and conversions are known to occur through a reactive metalcarbene intermediates with the release of dinitrogen (Fig. 1) when diazo reagents reacts with the hydrocarbon [23].



**Fig. 1. Metal Catalysed Carbene Insertion from Diazo-compound**

*Nakamura et al* reported the mechanism for rhodium-based catalysts which was already reported experimentally for the Cu and Ag based (coinage-metal) catalysts [24-26]. However, *Buchner et al* proposed that during the proceedings of the

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chemical reaction a cyclopropanation-derived norcaradiene intermediate (Fig.2) is formed that can be further evolved/formed when the chemical reaction is preceded through a cycloheptatriene.

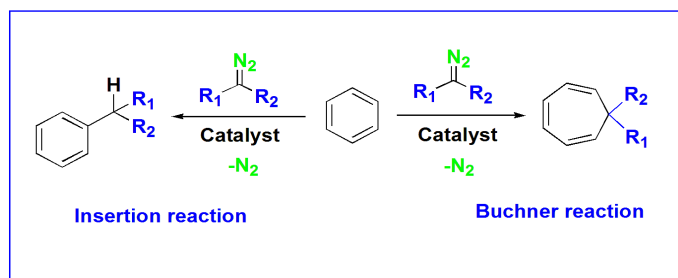


Fig. 2. Presentation of Insertion and Buchner reactions

Shechter and Livant separately had reported that in the presence of  $\text{Rh}_2(\text{OAc})_4$  catalyst, the metal-catalyzed functionalization of benzene because of the formal insertion of the carbene unit into the C–H bond (Fig.3) that can undergoes a 1,2- hydrogen shift to give the target molecule [27].

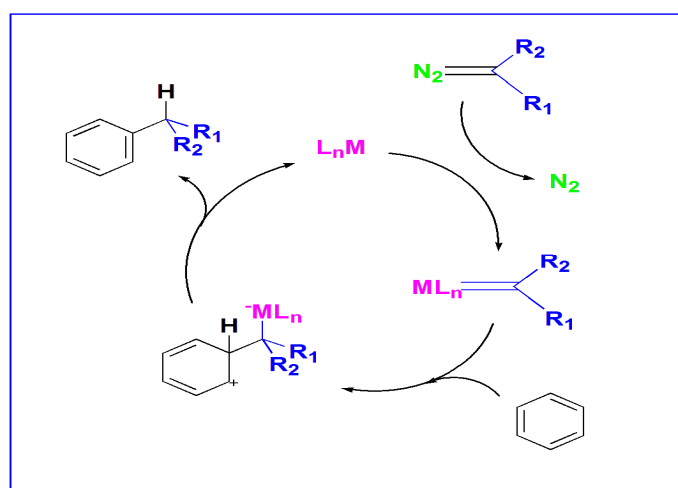


Fig. 3. Rh catalysed CH insertion

Gold was discovered as a catalyst for the transfer of the  $\text{CHCO}_2\text{Et}$  group from ethyl diazoacetate ( $\text{N}_2\text{CHCO}_2\text{Et}$ , EDA) to several saturated and unsaturated substrates in the presence of  $\text{IPrAuCl}$  ( $\text{IPr} = 1,3\text{-bis-}(\text{diisopropylphenyl})\text{imidazol-2-ylidene}$ ) as a silver based catalyst. The tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate is used as the main halide scavenger [28]. Hashmi *et al* (Fig.4) have proposed interesting mechanistic studies on gold-based transformations which may involve the vinylidene intermediates in C–H bond functionalization reactions [29].

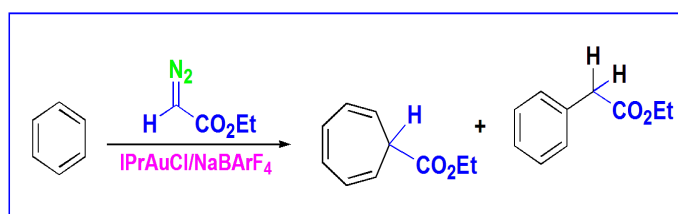


Fig. 4. Gold based catalytic system

*D F Taber et al* have reported (Fig.5) that rhodium (II) acetate mediate an intramolecular C–H insertion smoothly to give five-membered-ring formation with the retention of configuration. [30].

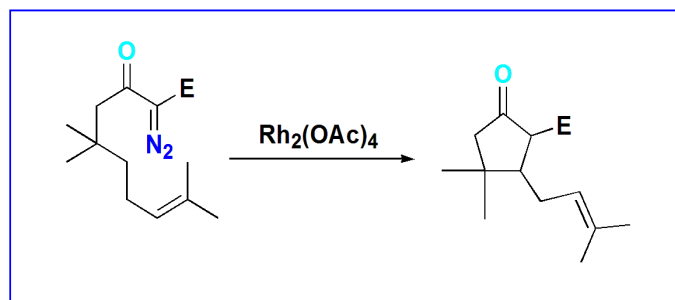


Fig. 5. Rh catalysed CH insertion

*J C Wang et al* examined that the reactivity of 1,4-cyclohexadiene with methyl phenyldiazoacetate (Fig.6) towards intermolecular carbene C–H insertion in the presence of 1 mol%  $[\text{Ir}(\text{TTP})(\text{CO})\text{Cl}]$  at room temperature for 24 h [31].

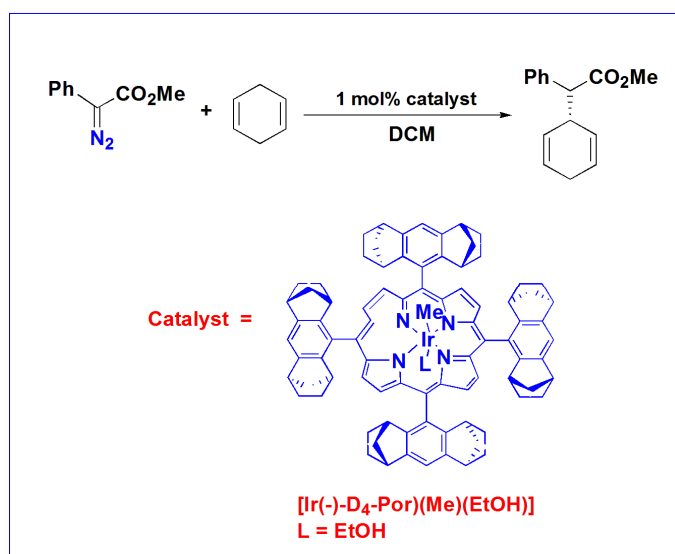


Fig. 6. CH insertion reaction catalysed by iridium porphyrins

*L A Clarke et al* (Fig.7) have recently reported an efficient and highly enantioselective copper mediated C–H insertion reactions of 2-sulfonyl-2-diazoesters in order to prepare thiopyrans and/or sulfolanes, and 2-sulfonyl-2-diazoketones to give cyclopentanones [32].

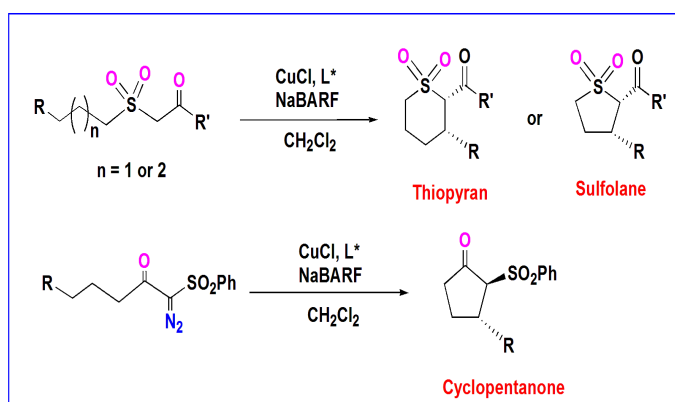


Fig. 7. Cu catalysed CH insertion reactions

*M P Doyle* reported (Fig.8) that the dirhodium (II) catalysts for intramolecular carbon-hydrogen insertion reactions of diazo carbonyl compounds has been found to have a significant synthetic achievement.  $\beta$ -Keto- $\alpha$ -diazo esters, phosphonates, and sulfones [33].

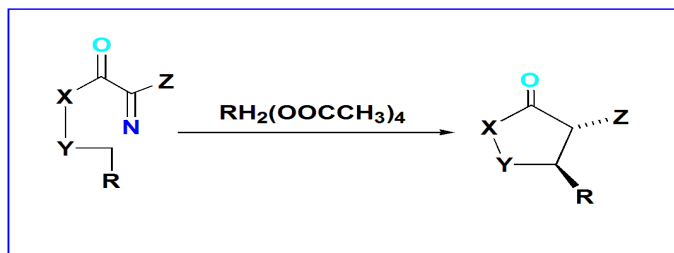


Fig. 8. Rh catalysed CH insertion reaction

Teyssie *et al* (1981) reported that the first example of successful insertion into a C-H bond in the presence of a rhodium (II) carboxylate catalyst. Based on this, *C N Slattery et al* reported a list of reactions involving successful insertion into a C-H bond (Fig.9) in the presence of a rhodium (II) carboxylate catalyst [34].

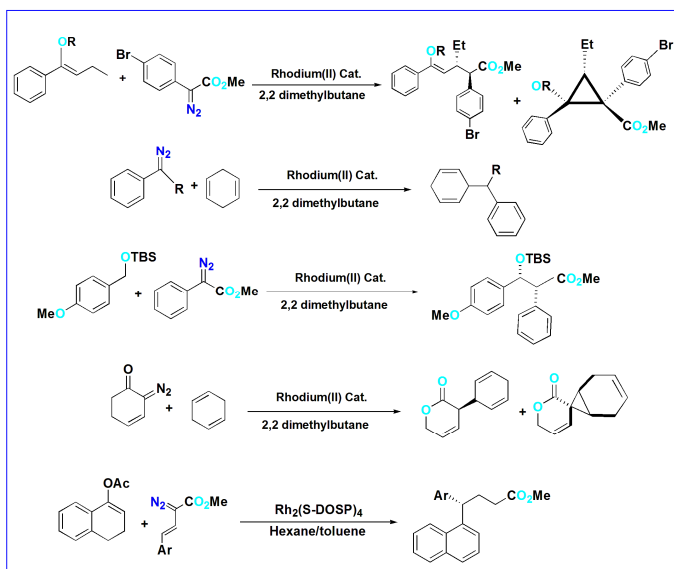


Fig. 9. Rh catalysed CH insertion reactions

*P Lahuerta et al* showed an interest in *ortho*-metalated Rh(II) carbene-transfer reactions. These reactions have centered on intramolecular cyclopropanation and C-H insertion reactions. So, they study by examining the possibility of effecting catalytic cyclization with *t*-butyl-2-diazo-3-oxoundecanoate in the presence of Rhodium (Fig.10) based catalysts at 100°C [35].

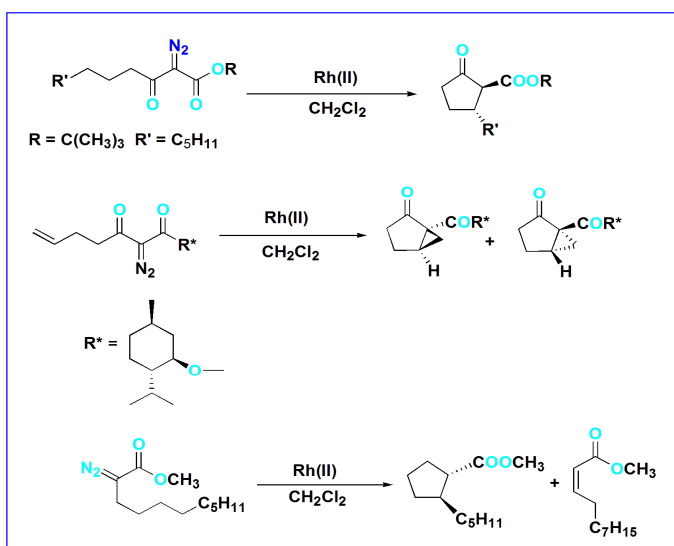


Fig. 10. Ortho-metalated rhodium(II)-catalyzed reaction

*M Ito et al* reported that the first catalytic asymmetric intramolecular i.e 1,6-C-H insertion reaction of  $\alpha$ -diazo esters in presence of dirhodium (II) tetrakis[N-phthaloyl-(S)-tert-leucinate],  $Rh_2(S-PTTL)_4$ . The C-H insertion reaction is proceeded in a chemoselective manner to give 2-alkenyltetrahydropyran-3-carboxylates (Fig.11) with a perfect cis diastereoselectivity [36].

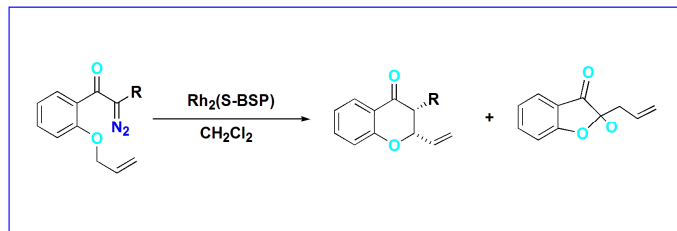


Fig. 11. Rh catalysed CH insertion reaction

*C N Slattery et al* reported (Fig.12) an Asymmetric copper-catalysed intramolecular CH insertion reactions of  $\alpha$ -diazosulfones in the presence borate additives like NaBARF and KBARF which were found to be the most effective additives for the procedure of highly enantioselective syntheses in short reaction rates and high efficiency [37].

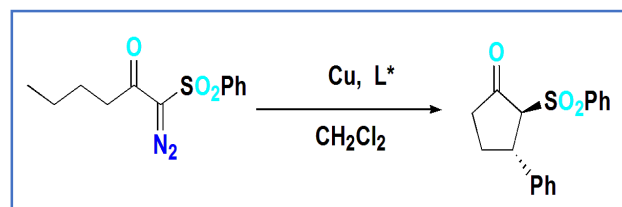


Fig. 12. Cu catalysed CH Insertion reaction

## Conclusion

In this review article, the different types of Chemical reactions have been presented to illustrate the CH insertion. The process of CH insertion was depicted by a number of chemical processes were found to carry out easily under the influence of transition elements as catalysts. The coordination compounds of transition elements were reported to play an important role in both CH insertion as well as functionalization. Currently, the CH insertion and functionalization is a vast and useful field of chemistry. However, in this field more and more research is still required to discover and invent new catalysts, methods, techniques for CH insertion as well as functionalization.

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