

C-H bond activation using palladium catalysts, iridium catalysts, and iron catalysts

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Abstract— Recently, there have been a large number of reports on “C-H bond activation reaction”. C-H bond activation is a methodology for directly forming carbon-carbon bonds by activating a carbon hydrogen bond, which is the most fundamental linkage in organic chemistry. Traditional cross coupling reactions have been one of the most useful synthetic methods for the formation of carbon carbon bonds. However, the cross coupling reaction requires extra procedures for preparing organic halides (or triflates) compounds, and organic boron or metal compounds. On the other hand, the C-H bond activation can reduce these procedures, thus making this reaction a cost-effective and ecofriendly system.

Keywords— Carbon-Hydrogen bond activation, cross coupling, Carbon-carbon bond, synthetic methods, organic chemistry

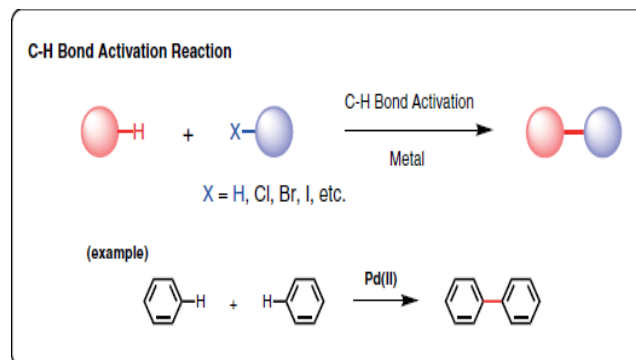
I. INTRODUCTION

Organic chemists struggle to develop and build use of capable and atom economical methodology for the elaboration of advanced structures from simple and promptly gettable precursors. Over the history 20 years, unbelievable strides are created within the functionalization of carbon-hydrogen bonds, arguably the foremost current “functional group” in chemical science. Our research done with the our knowledge and chemistry department of saurashtra university and R.K. university. Direct carbon-hydrogen activation (in distinction to metal-carbenoid elicited carbon -hydrogen insertion) has its roots within the pioneering work of Shilov, Bercaw, Bergman, Crabtree, Murai, and goldman, chemical analysis back to the Seventies and Eighties.¹ Formally, it needs insertion of a transition metal (usually metallic element, Ir, Rh or Pd) across a strong carbon -hydrogen bond (90-105 kcal/mol) to make a brand new, weaker C-Metal bond (50- eighty kcal/mol), followed by creation of a completely unique C-C bond (Scheme 1).¹

A central goal within the progress of any new methodology is artificial utility, one that has, for the foremost half, eluded this field. The presence and inherent stability of carbon -hydrogen bonds makes the development of synthetically valuable processes particularly intimidating.

II. RELATED WORK

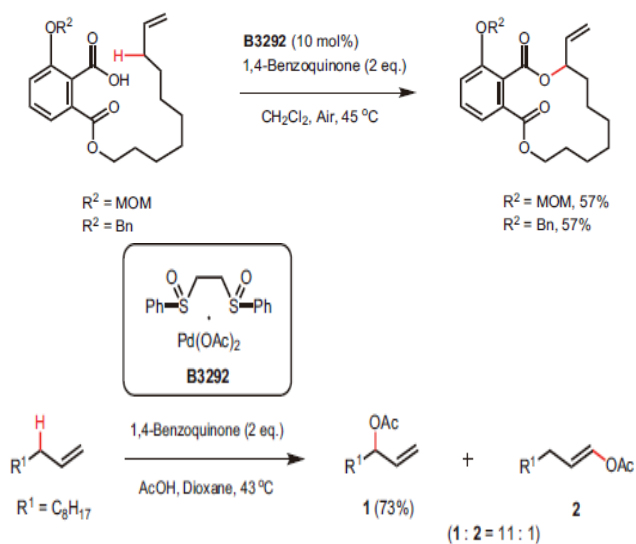
C-H bonds generally have relatively high energy therefore the formation of a carbon-carbon or carbon-heteroatom bond by dissecting C-H bonds has been believed to be difficult. In 1993, Murai et al. reported the direct addition of C-H bonds of aromatic ketones to olefins in the presence of a catalytic amount of carbonyl(dihydrido)tris(triphenylphosphine)ruthenium(II) (C2251).¹ Since then, numerous examples of C-H bond activation have been reported. The reaction above proceeds without using halogenated compounds and organic boron or organic metal compounds. Thus, this system is cost-effective and eco-friendly. In general, palladium(II), rhodium(I), iridium(I), ruthenium(II), copper(II), and iron(II) are widely used in C-H bond activation.



III. METHODOLOGY

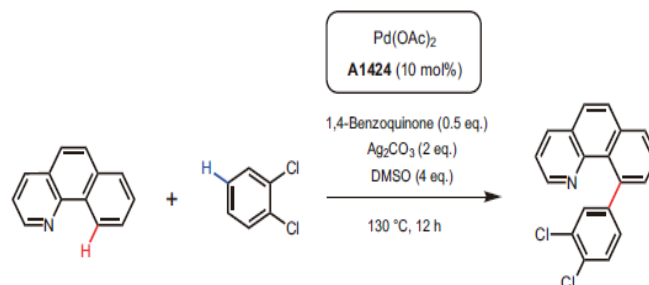
There are a number of reports on C-H bond activation using these catalysts in the presence of appropriate ligands and activating reagents. In this brochure, some examples of C-H bond activation using palladium catalysts, iridium catalysts, and iron catalysts are shown as below.

Pd(II) Catalysts



1) Regio-selective Coupling Reaction of 7,8-Benzoquinoline and Arene Compounds Sanford *et al.* have reported the direct coupling reaction of 7,8-benzoquinoline and arene compounds using palladium acetate(II) (**A1424**).² In this reaction, a nitrogen atom of 7,8-benzoquinoline functions as a directing group to allow it to selectively introduce arenes at the C-10 position. Moreover, arene compounds also react with 7,8-benzoquinoline at the least sterically hindered positions. In this reaction system, 1,4-benzoquinone functions as a reaction promoter, and silver(I) carbonate oxidizes the generated Pd(0) species, which forms the Pd(II) / Pd(0) catalytic cycle.

2) Allylic C-H Oxidation using “White Catalyst” 1,2-Bis(phenylsulfinyl)ethane palladium(II) diacetate (**B3292**) is a palladium catalyst, which was developed by M. C. White *et al.*, and named “White catalyst” after the developer. For an example of its characteristic reactivity differing from other homogeneous palladium catalysts, the allylic C-H oxidation reaction has been reported, in which an acetoxy group is introduced regioselectively into the allylic position.³

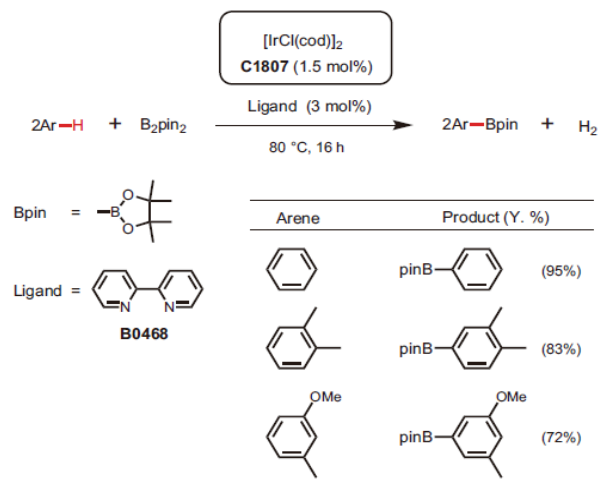


Moreover, White *et al.* have also reported the macrolactonization reaction of ortho-substituted salicylic acid substrates, applying the reaction into intramolecular allylic C-H oxidation, in which the corresponding 14-membered ring macrolides are obtained in moderate yields.⁴

Ir(I) Catalyst

Miyaura, Ishiyama and Hargwig *et al.* have reported the direct C-H borylation in 2002.

5) This reaction is the most famous and practical example of C-H bond activation using iridium catalysts. Aryl borates had been synthesized by the reaction of aryl lithium or magnesium reagents with trialkyl borates so far, however, their method allowed a one-step preparation of alkyl borates in a simple manner.



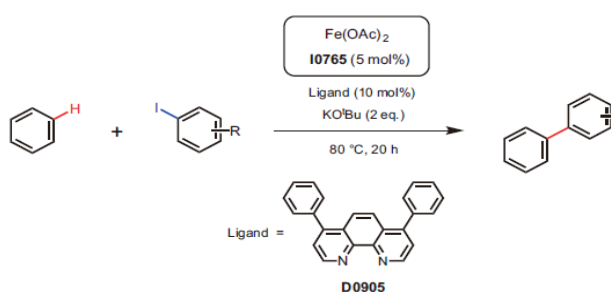
IV. RESULTS AND DISCUSSION

Fe(II) Catalyst

Including palladium catalysts, which are frequently used for the Suzuki-Miyaura coupling reaction, transition metal catalysts, such as nickel or platinum, have been widely used for organic synthesis. However, the percentages of these metals in the earth's crust are extremely small, and their prices are rather expensive.⁶ On the other hand, iron

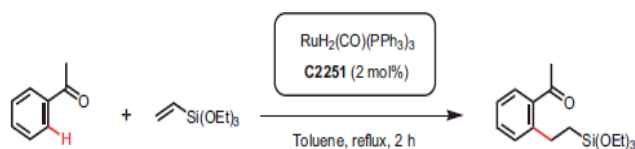
is abundant and less expensive, and therefore, more and more chemists have focused their attention to organic synthesis using iron compounds. As a catalyst, cross-coupling reactions using iron catalysts have been reported.⁷⁾ For an example of C-H activation using iron catalysts, Charette *et al.* have reported the direct coupling reaction of benzene with aryl iodides using iron(II) acetate (**I0765**).⁸⁾ This reaction is highly cost-effective and environmentally friendly in the sense of using an iron catalyst, which is less expensive, and therefore, further development and applications are expected from the point of green chemistry.

V. CONCLUSION AND FUTURE SCOPE



Aryl iodide	Product (Y. %)
	(89%)
	(60%)
	(93%)
	(40%)
	(79%)

In the past a little number of years, many teams have addressed vital aspects of carbon-hydrogen activation.



As evident, new developments within the areas of reactivity, substrate scope, purposeful cluster tolerance and

enantioselectivity are pushing the boundaries of carbon-hydrogen activation; but, systems of great sensible utility are simply begin to seem. The attract of this new and increasing field, definitely spur raised academic and industrial attention, and improved protocols for fascinating and synthetically applicable reactions are possible to still seem.

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