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ORGANOMETALLIC C–H BOND ACTIVATION AND FUNCTIONALIZATION: MECHANISMS, CATALYTIC STRATEGIES, AND SYNTHETIC APPLICATIONS

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Abstract: *The selective activation and functionalization of carbon–hydrogen (C–H) bonds represents an important area of organometallic chemistry because it provides opportunities to transform relatively unreactive C–H bonds directly into synthetically valuable functionalities. This paper examines the development, mechanistic foundations, and catalytic applications of organometallic C–H bond activation, with particular emphasis on transition-metal-mediated processes. The discussion traces the historical evolution of the field from early observations of electrophilic and oxidative activation to the development of increasingly sophisticated catalytic systems. Particular attention is given to electrophilic C–H activation and oxidative addition, highlighting their mechanistic relationships rather than treating them as completely independent pathways. The Shilov system is examined as an important example of platinum-mediated alkane activation and functionalization, involving C–H activation, oxidation, and subsequent product-forming steps. The paper further discusses oxidative addition of aromatic and aliphatic C–H bonds and the contribution of transition-metal complexes containing platinum, ruthenium, rhodium, and iridium to the development of C–H activation chemistry. Catalytic applications involving carbonylation, insertion reactions, site-directed functionalization, and alkane dehydrogenation are also considered. The discussion demonstrates that metal electronic properties, ligand environments, substrate structure, directing groups, and reaction conditions collectively determine the mechanism, selectivity, and catalytic efficiency of C–H functionalization. Overall, organometallic C–H activation provides an important platform for developing more direct approaches to molecular modification, although improvements in catalyst stability, selectivity, efficiency, and practical applicability remain important areas for continued research.*

Keywords: *C–H bond activation; organometallic chemistry; C–H functionalization; oxidative addition; electrophilic activation; transition-metal catalysis; Shilov system; alkane functionalization.*

1. INTRODUCTION

The un-functional group is the carbon-hydrogen bond. The conventional picture of organic molecules does a good job of illustrating its special place in organic chemistry; in this picture, the lack of any other link indicates that C-H bonds are present. The "invisibility" of C-H bonds is a result of their nonreactivity and pervasiveness. Considering these features, it's easy to see how the capacity to selectively functionalize C-H bonds may be the most versatile and effective transformation class in organic synthesis, if it were fully developed. If this possibility comes to fruition, it has the ability to radically alter the process of creating organic molecules, from the simplest methanol to the most complex natural or synthetic compounds. The most recent and prominent studies in this area are reviewed here, with an emphasis on the work that has been done to activate C-H bonds via "organometallic routes" (i.e., methods that include the production of a bond between carbon and a metal core).

2. THE PRELIMINARY SCENES (AND C-H ACTIVATION)

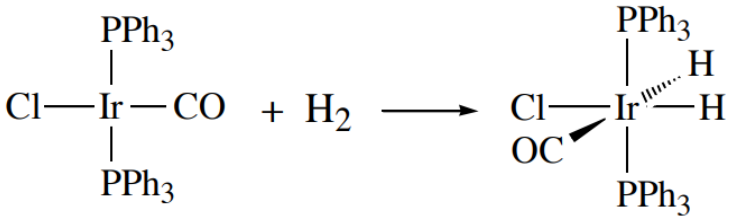
There is a history of systems based on transition metals activating C-H bonds. This is something that bacteria have been doing for billions of years! C-H activation by transition metals has been known about since at least 1898, according to Grushin, Thorn, and co-authors, who are more self-aware in their discussion of "modern" chemistry.

There were no glaring advancements in C-H activation during the inorganic/organometallic chemistry revolution of the 1950s and 1960s. However, other groundbreaking findings did point (to the keenest observers) in the direction of potential pathways for C-H activation. The H_2-bond is most similar to the C-H bond in polarity and bond strength. Several metal ions were reduced by Cu after Halpern discovered in 1955 that Cu^{2+} could heterolytically cleave H_2 (eq 1) H_2.

$$Cu^{2+} + H_2 \rightarrow [CuH]^+ + H^+ \quad (1)$$

Not long after, it was discovered that a number of other metals, such as silver(I) and mercury (II), had the same properties.

Following the oxidative addition of H_2 to Ir $(PPh_3)_2(CO)Cl$ (eq 3.2).



(2)

Vaska maintained vehemently that the reaction was really oxidative (rather than just a transition from I to III oxidation state), and this perspective has persisted to a considerable extent to this day.

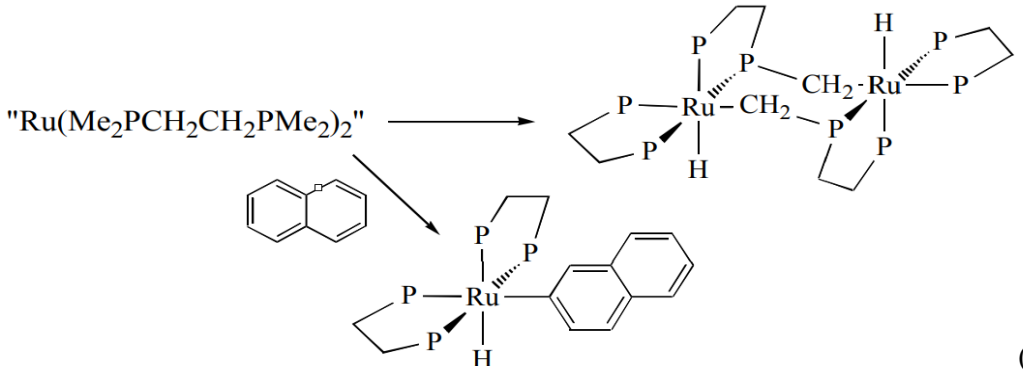
The two most common methods of activating C-H bonds by transition metal complexes nowadays have their roots in these two processes that activate dihydrogen electrophilically and oxidatively, respectively. The two are really very much related, despite the common belief that their motivations are diametrically opposed. It was first thought that the electrophilic activations would take place via the coordination of H_2 followed by the depletion of H^+

$$Cu^{2+} + H_2 \rightarrow [Cu(H_2)]^{2+} \rightarrow [Cu(H)]^+ + H^+ \quad (3)$$

It is now known that the oxidative addition of hydrogen often goes via an intermediate dihydrogen complex (eq 3.4), or at least a transition state that is extremely similar to one.

$$M + H_2 \rightarrow M(H_2) \rightarrow M(H)_2 \quad (4)$$

Therefore, there is more in common across these chemical routes than there is to differentiate them. Many people believe that Chatt was the first to record an instance of "C-H activation" by a complex of transition metals. The formation of Ru(0) $(dmpe)_2$ caused the activation of a C-H bond in either the naphthalene C-H bond or the phosphinomethyl group of the ligand (eq 5).



(5)

These reactions exemplify oxidative addition, similar to Vaska's finding in equation 2. It was stated that Wilkinson had developed a hydrogenation catalyst about the same time as Chatt. The catalytic cycle's mechanism, which uses Rh(I) and Rh (III) intermediates in turn, includes the addition of H_2 and the reductive removal of a C-H bond, according to modern terminology. The use of platinum

catalysts in olefin hydrogenation was further expanded upon by Shilov. After realizing that the reversibility of the C-H elimination from a Pt alkyl to provide Pt (II) was a crucial step in this reaction, it was studied further. Equation 6 shows that Pt (II) might react with C-H bonds, and in the presence of Pt (II), there was an observed H/D exchange between methane and D_2O.

$$CH_4 + D_2O \xrightarrow[D_2O\,/\,CH_3CO_2D]{K_2PtCl_4} CH_3D + HDO \quad (6)$$

An electrophilic substitution was proposed as the potential pathway for the process to take place (eq 7).

$$Pt(II) + R\text{-}H \rightarrow Pt(II)\text{-}R + H^+ \quad (7)$$

Similar to the modalities of H_2 addition mentioned earlier, the reactions of C-H bonds with the nucleophilic $Ru(dmpe)_2$ and the electrophilic Pt (II) species may seem to be influenced by completely separate factors. So, C-H bond activations are often categorized as either electrophilic or nucleophilic (oxidative addition). The similarities between the two types of C-H activation are substantial, albeit not as great as those between the associated H_2 activation modes. The presence of a σ-bond complexed intermediate seems to be a common pathway for both reactions. The fact that full oxidative addition (and subsequent deprotonation of the metal hydride) is the mechanism by which some (if not all) purportedly electrophilic activations occur is even more astonishing. On the flip side, Crabtree identified an early instance of alkane activation that included "oxidative" addition to a very electrophilic cationic iridium complex.

There is, therefore, no dichotomy in the connection between electrophilic and oxidative activation. For the sake of structure, we will reluctantly maintain this difference in the parts that follow. Workers in the field may have been so concentrated on one side of the divide that the separation has taken on a life of its own, serving as an effective organizing tool. This difference is becoming more and more blurry, and its utility has probably been outlasted, as we hope the reader will see in the following debate.

3. SYSTEMS THAT ARE "ELECTROPHILIC"

Shilov made significant progress on his previous study of C-H activation with Pt (II) (eq. 6) and published it in 1972. Selectively oxidized species methanol and methyl chloride were produced when Pt (IV) was added to the water-based reaction of $PtCl_4^{2-}$ with methane. Unfortunately, this reaction, as shown in eq 8, is stoichiometric in Pt (IV) but catalytic in Pt (II).

$$CH_4 + PtCl_6^{2-} + H_2O\,(Cl^-) \xrightarrow[H_2O,\ 120\ ^\circ C]{PtCl_4^{2-}} CH_3OH\,(CH_3Cl) + PtCl_4^{2-} + 2\,HCl \quad (8)$$

Though it is not feasible to use platinum as a stoichiometric oxidant, this "Shilov system" from thirty years ago is still one of the few catalytic systems that can selectively functionalize alkanes under moderate circumstances. Because of its uniqueness and the fact that this transition had never been seen before, "Shilov chemistry" has assumed a major position in the study of C-H activation. It is worth mentioning that researchers from outside the Soviet Union did not immediately pursue Shilov's promising finding in the early 1970s. Scientists from the Soviet and Western blocs were unable to communicate and trust one another due to the political atmosphere of the period, which may explain why this major breakthrough was widely recognized so late. The Western world did not "rediscover" Shilov's work until the 1980s.

A large portion of the "Shilov Chemistry" literature focuses on trying to pin down the exact process that causes the Shilov reaction (eq. 8). Shortly after reporting the oxidation, Shilov offered a plausible mechanical design for the catalytic cycle. The first stage of this cycle involves reacting Pt(II) with an alkane to produce an intermediate called methylplatinum(II). In the second step, a methylplatinum(IV) species is formed by oxidizing the result of this C-H activation process. To create the functionalized product and return the Pt center to Pt (II) in the last step, one might use reductive elimination with coordinated water or chloride and the Pt (IV) methyl group, or one could use nucleophilic assault at the carbon with an external nucleophile (H_2O or Cl^-). There has been strong experimental evidence for this overarching process within the last 20 years.

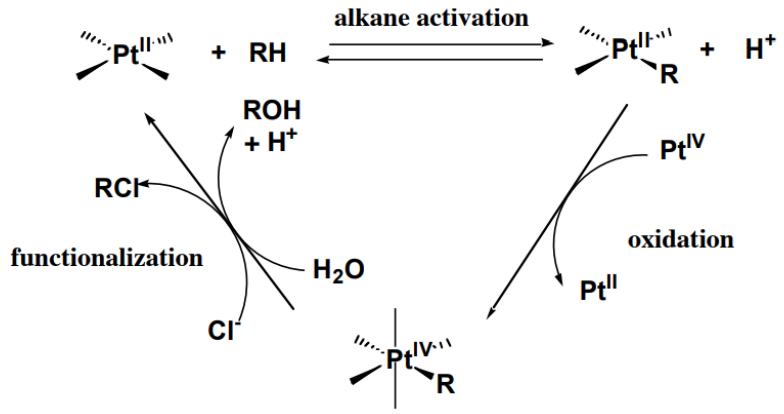
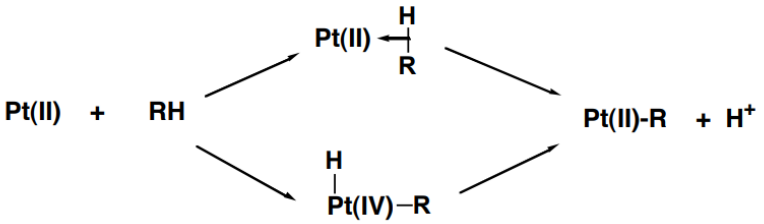


Figure 1 A possible process for the alkane oxidation by Shilov that is accelerated by platinum

Other comparable Pt-based C-H functionalization systems are believed to be based on the cycle depicted in Figure 1. Nevertheless, the shown cycle is very generic, and the specific processes of the three separate steps—C-H activation, oxidation, and functionalization—may vary between systems. As an example, there has been a lot of discussion on the exact mechanism by which platinum (II) activates C-H bonds; some have proposed an electrophilic route, while others propose an oxidative addition followed by platinum deprotonation (eq 9). Model platinum(II) systems, especially those with nitrogen ligands, have recently had experimental data offered in favor of the oxidative addition mechanism. The production of stable Pt (IV) alkyl hydrides from Pt (II) species reacting with alkanes proves that oxidatively adding C-H bonds to Pt (II) is a real technique to activate alkanes. The data obtained from these model systems, however, does not prove that platinum-catalyzed alkane functionalization events entail oxidative addition. It is possible that the specific platinum (II) species at work in the real-life Shilov system reacts via electrophilic activation. Research into the activation of methane by Pt $(H_2O)_2Cl_2$, the catalyst believed to be active in the Shilov process, has shown that the barriers to both processes are very comparable.



(9)

Much mechanistic research has been focused on the oxidation and functionalization phases of the Shilov process, which are equally intriguing. Importantly, Pt (IV) functions as an external oxidant, as was shown by the elegant labeling studies conducted by Labinger and Bercaw. This significant finding paves the way for the functionalization to make use of a less expensive oxidant. To that purpose, several oxidants such as SO_3 (discussed further below), Cl_2, H_2O_2, and O_2/heteropolyacids or O_2/Cu (II) have been documented by researchers in recent years as being able to accomplish this change. No economically feasible technology has been produced to yet, and overall, success has been minimal. Nucleophilic assault at the carbon is what ultimately leads to the creation of the carbon-heteroatom bond and the product in the Shilov cycle. The most convincing evidence comes from research showing that model systems exhibit stereochemical inversion at carbon. Additionally, there is strong evidence that the creation of carbon-heteroatom bonds involves a nucleophilic assault at five-coordinate Pt (IV) rather than six-coordinate Pt (IV).

A major improvement to the Shilov system didn't show up until 1998. Equation 10 shows that a platinum (II) bipyrimidine catalyst in concentrated sulfuric acid preferentially converts methane to methyl bisulfate, as found by researchers at Catalytica. This process, which typically employs SO3 as the oxidant, reached an astounding 72% yield, with 89% methane conversion and 81% selectivity.

$$CH_4 + 2\,H_2SO_4 \xrightarrow{(bpym)PtCl_2} CH_3OSO_3H + 2\,H_2O + SO_2 \quad (10)$$

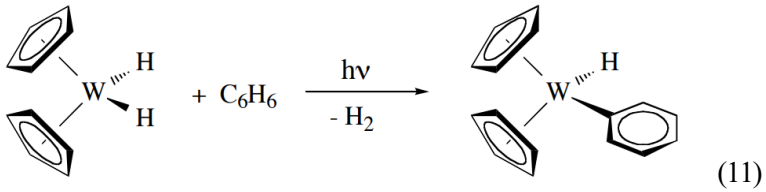
After looking into how this reaction works, scientists came up with a broad plan that is similar to the one shown in Figure 1 for the Shilov reaction. Recently, computational approaches were used to investigate the intimate mechanism of the C-H activation phase that creates the Pt (II)-methyl intermediate. The results showed that an electrophilic mechanism, rather than oxidative addition, was preferred for C-H activation. The oxidative addition route was preferred over the electrophilic one for the analogous complex $(NH_3)_2PtCl_2$, which was shown to be a more active but less stable catalyst for methane oxidation under comparable circumstances. Different computations find different results when considering cationic platinum species or full ion pairs, and when different ligands are substituted with methane. Consequently, the solvent medium should impact the C-H activation step's intimate mechanism in platinum-catalyzed alkane oxidation processes, an issue that is challenging to address computationally. Obviously, this mechanism is still up for debate when it comes to Pt (II) C-H bond activation, and researchers are constantly comparing the two paths.

Catalytica described a comparable system before the same researchers revealed the Pt (II)/H_2SO_4 system Hg (II)/H_2SO_4 apparatus for the oxidation of methane. Hg (II) cannot participate in an oxidative addition pathway, so the electrophilic method of C-H activation was chosen. Nevertheless, Sen and colleagues have proposed an alternate electron transfer method that is compatible with the experimental findings. This approach involves Hg (II) acting as a one-electron outer-sphere oxidant, and it merits consideration for this reaction.

4. ADDING OXIDATIVE GROUPS TO C-H BONDS

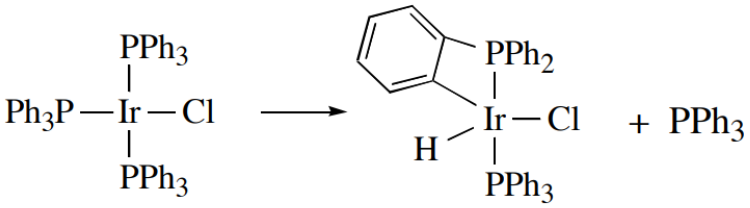
At the same time that Shilov was pioneering work on electrophilic systems, other labs' findings seemed to indicate the polar opposite as the best way to activate C-H bonds. Following Chatt's 1965 finding of the reactions of the very electron-rich species $Ru(dmpe)_2$ (eq. 5), many further instances of seemingly electron-rich metal centers that could oxidatively add C-H bonds were identified.

Intramolecular addition of aryl or alkyl ligand C-H bonds was common in these first instances, as was the addition of aryl C-H bonds in the Chatt system in equation 5. As an example, Green found that the addition of benzene C-H bonds occurred as a consequence of the photoelimination of dihydrogen from Cp_2WH_2 (eq. 11).

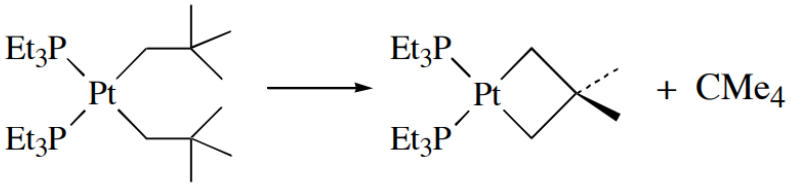


(11)

It was first identified and later shown to be rather common to cyclometalate aryl groups on ligands (eq. 12). Equation 13 shows that an aliphatic, distant C-H bond was added, as described by Whitesides.



(12)

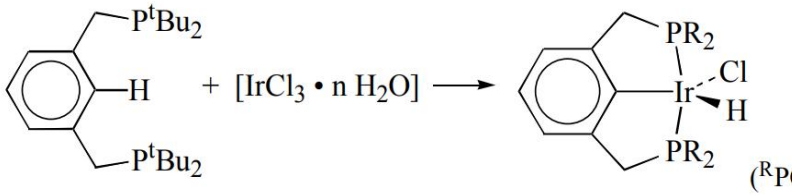


(13)

Although early examples of C-H addition did not necessarily involve metal centers that were abundant in electrons (refer to the W(II) and Pt (II) centers in equations 12 and 13), the nomenclature and nature of oxidative addition indicated that metal centers with more electrons were preferable. The fact that Chatt's $Ru(dmpe)_2$ example was the first of its kind likely gave it an unfair advantage, even if

it was an extreme situation. It is ironic since Roddick discovered later that $Ru[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2)]_2$, which is much less electron-rich than $Ru(dmpe)_2$, seems to be more reactive toward alkane and arene C-H bonds.

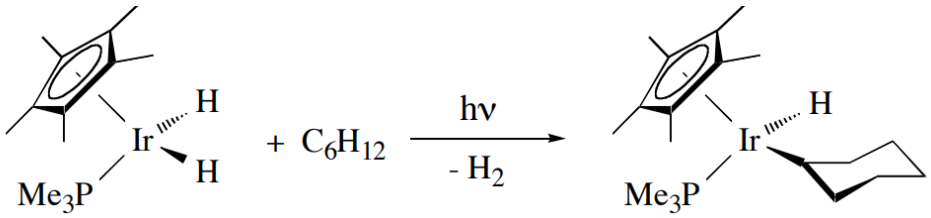
Shaw used cyclometalation to create extraordinarily stable ligands by taking advantage of the very favorable intramolecular activation of aryl C-H bonds.



(^{R}PCP)IrHCl (14)

An early example of what could be referred to as self-assembly was immediately shown with a variety of simple metal halide salts, such as Rh, Ir, Ni, Pd, and Pt, and the bisphosphine shown in equation 15 as having a tendency to undergo cyclometalation, resulting in the corresponding "^{R}PCP" tridentate ligated complexes. In the long run, this example and similar "pincer" ligands would serve a supplementary but still critical function in C-H activation. Also, the first instance of adding a C-C bond in a way similar to the C-H activations described here occurred as a result of the reaction of similar diphosphines that were methylated at the 2-position.

The first instances of intermolecular addition of alkane C-H bonds to produce stable alkyl iridium hydrides were reported in 1982 by Bergman and Graham, marking the apogee of these findings of intramolecular and intermolecular aryl C-H oxidative addition. The first instance of such reaction must undoubtedly be a watershed moment, and this innovation has rightfully become famous.



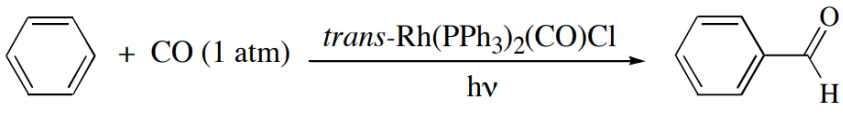
(15)

However, what might be the most crucial part of this piece is probably still being given the credit it deserves. In his research, Bergman discovered an unusual preference for C-H bonds. This Cp*Ir (PMe_3) (Cp* = η^5-C_5Me_5) The metal core exhibited a remarkable inclination towards breaking stronger C-H bonds, such as aryl bonds, which ranked higher than 2° and 3°. Many other researchers, including Graham, Jones, Flood, and Field, confirmed and expanded upon this finding. C-H addition kinetics and thermodynamics were shown to be more advantageous for less-substituted alkyl groups to transition metal complexes, at least for the late metals. We must not overlook the significance of this. To begin with, it enables transition metals to exhibit complementary selectivity for other chemicals that can cleave C-H bonds, as opposed to the majority of other reagents. In a lot of situations, this kind of selection is great. An example of a much-sought-after objective is the terminal functionalization of n-alkanes. In addition, the derivatized product may not be activated as easily as the alkane, which is a surprise selectivity for stronger C-H bonds. The C-H bonds in derivatized products are almost always weaker than those in the parent alkane. As a consequence, most species that may activate C-H bonds are selective for the products, leading to further transformations that are usually undesirable, such as the over-oxidation of methane to CO_2).

5. OXIDATIVE ADDITION OF C-H BONDS ALLOWS FOR CATALYTIC FUNCTIONALIZATION.

The CO and isonitrile insertion into C-H bonds

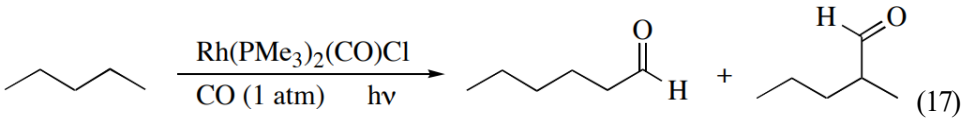
Carbonylations (e.g., hydroformylation and the Monsanto acetic acid process) are undoubtedly among the most significant of the several processes that use transition metal alkyls as intermediates. As a result, efforts to combine stoichiometric alkane C-H oxidative addition to CpML and other fragments into catalytic carbonylation cycles were made shortly after the original flurry of findings. None of these efforts were directly fruitful as far as we are aware. On the other hand, Eisenberg found out that Rh $(PPh_3)_2(CO)Cl$ photochemically catalyzed the carbonylation of benzene.



(16)

It was early recognized that three-coordinate d8 fragments were important for carbonylation since it was believed that this reaction would happen by photoextrusion of a ligand (either CO or PPh_3). Therefore, C-H activation by Rh $(PR_3)_2Cl$ seen it firsthand. Additional backing for the endeavors of the Rh $(PR_3)_2Cl$ After that, studies focusing on short timescales, such as low-temperature matrix photolysis and conventional kinetics, were conducted.

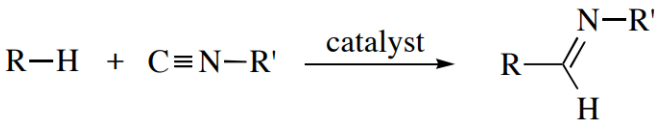
Being mindful of the fact that Bergman's Cp*Ir (PR_3) found that PMe_3 was better than PPh^3, studied the trimethyl phosphine analogue of Eisenberg's catalyst Rh $(PMe_3)_2(CO)Cl$ did carbonylate alkanes in addition to benzene, which was a major finding (eq. 17), and it was also slightly more effective for carbonylation of benzene. Curiously, n-alkanes could be carbonylated with regioselectivity for the terminal position using short-wavelength light, but branching aldehydes were mostly produced by longer-wavelength light.



(17)

Field and Goldman postulated that two separate processes would drive this response. By first photoeluting CO and then adding C-H, the long-wavelength method activated C-H bonds. It was suggested that the short-wavelength process started with an intact, four-coordinate, photoexcited species undergoing direct C-H oxidative addition; a second photon was then needed to trigger the migration of alkyl to carbon. In light of these results, one may tweak the setup so that the short-wavelength mechanism produced much higher turnover rates, quantum yields, and selectivity. Ford and Bitterwolf's TRIR investigations provided significant evidence for the duality of mechanisms.

Light or coupling with a secondary reaction are required to achieve substantial catalytic yields when carbonylating hydrocarbons, since this is an endoergic process (especially for alkanes but also for arenes). However, the exothermic insertion of isocyanides is a similarly related process. Although Cp*Rh (NCR) and TpRh (NCR) fragments may activate C-H bonds, which has been used to uncover many details about the mechanism and selectivity of these compounds, these species cannot be catalytically functionalized. On the other hand, Jones has created a number of systems that can catalyze intramolecular insertion to produce indoles and aldimines (eq. 18). The d^8 metal centers that hold mono- and bidentate phosphines provide the basis of these systems; the metal centers in question are Fe (0), Ru (0), and Rh(I).

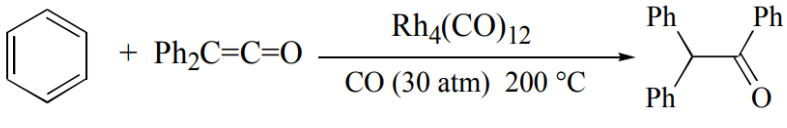


(18)

The dearth of catalytic events is noteworthy when put in the context of the extensive C-H activation chemistry of Tp- and Cp-containing complexes, as mentioned before. Several unsaturated intermediates would surely be formed along pathways for desired catalytic reactions. The thermodynamics of C-H addition is favored by the incapacity of CpM fragments to adopt stable unsaturated configurations, as mentioned earlier, in comparison to complexes containing monodentate ligands. It is plausible to assume that the same elements that promote stoichiometric reactions may hinder catalytic reactions due to the fact that they increase the energy of coordinatively unsaturated intermediates, which are crucial in catalysis.

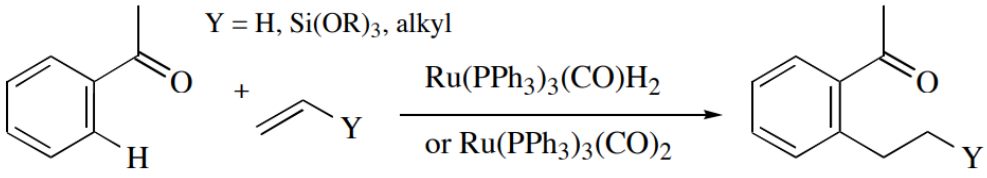
Saturated C-C bonds being inserted into C-H bonds

Olefin oligomerization and polymerization catalysts are only two examples of the numerous transition-metal based systems that exhibit an extremely low barrier to the introduction of unsaturated olefins or other compounds into metal-carbon bonds. Given this, the few instances of unsaturated species being introduced into alkyl C-H bonds (i.e., causing alkyl C-H addition across a double or triple bond) may come as a surprise. But there has been a lot of success with inserting into vinyl and aryl C-H bonds in the last ten years. One possible explanation for the noticeable difference between sp^2 and sp^3 C-H bonds is that sp^2 bonds are often more reactive. It is likely that sp^2-hybridized carbon atoms also prefer other stages of the catalytic cycles, especially C-C reductive elimination. Equation 19 shows that hydro phenylation of diphenylketene was one of the first examples of this kind of reaction.



(19)

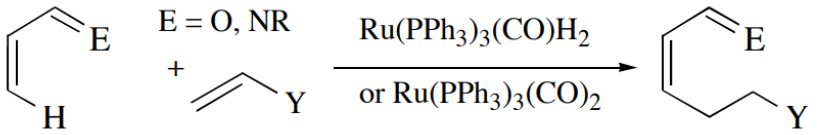
A major step forward in this area; Ru $(PPh_3)_3(CO)_2$ and Ru $(PPh_3)_3(CO)H_2$ were discovered to facilitate the addition of olefins to aromatic ketones' ortho C-H bonds (eq 20).



(20)

The vast majority of our current understanding of unsaturated insertion into C-H bonds has arisen from this reaction (1f). While we will use this study as an example of this kind of reaction, we are very cautious about making broad assumptions about different catalyst systems.

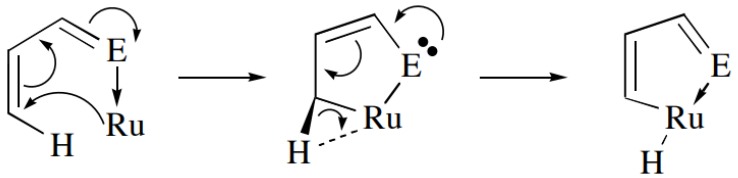
The system of equation 20 has been expanded to include the addition of alkynes and olefins, and more significantly, to a wide variety of substrates that have a directing group to a sp^2 C-H bond (either N- or O-coordinating) (eq 21) (1f).



(21)

With both reagents, yields may be rather high, albeit not quantitative. So, as pointed out by Pfeffer (1g), this is the most useful example of catalytic C-H bond functionalization at the moment in terms of practical application.

'Directing' groups conjugated with the π-system of the C-H bond reacting (such as carbonyl or imine) greatly enhance Ru-catalyzed insertions. Bringing the C-H bond close to the metal center (i.e. lowering the entropic cost of C-H addition) is definitely not the only intricate function that this group performs. According to Morokuma's density-functional theory calculations, one potential function is to promote C-H addition via a transition state, as shown in equation 21. It should be noted that although the end outcome remains same, equation 22 depicts a distinct process compared to the one often used for basic C-H oxidative addition. In this regard, it should be noted that not all substrates converted by this system contain the diene pattern as stated in equation 21. There are only a few recorded cases where even sp^3 C-H bonds are added.



(22)

After C-H addition, two possible mechanisms for olefin insertion might be considered: (a) inserting into the Ru-C bond that forms, or (b) inserting into the Ru-H bond that forms. The corresponding reductive elimination (C-H or C-C, respectively) would then occur in each instance. The hydrometalation route (b) and the general process shown in Figure 5 have been supported by Murai's strong evidence, which is summarized below. (Remember that a zerovalent ruthenium species, like, maybe, may be formed from the dihydride precursor.) Ru $(CO)_n(PPh_3)_m$).

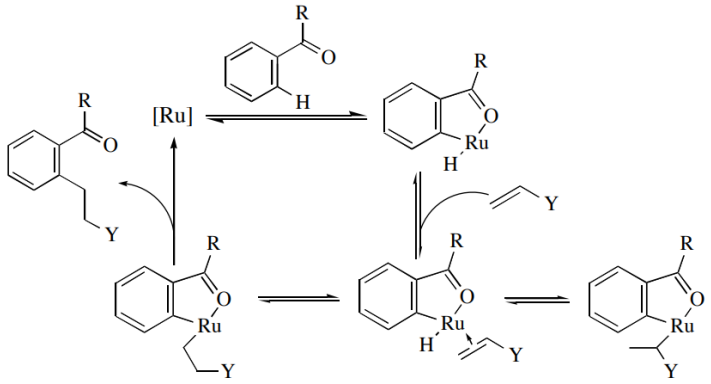
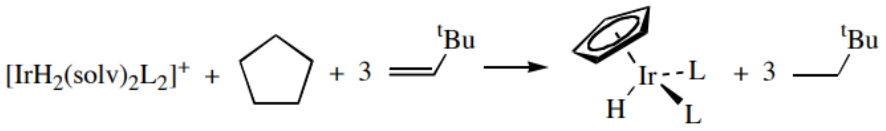


Figure 5. Murai came up with a method for adding C-H bonds to olefins using a Ru (0) catalyst that he called the "site-directed" addition.

When it comes to olefins, methyl benzoate does not couple; nonetheless, $C_6D_5CO_2CH_3$ exchanges hydrogen ions with vinylic protons and ortho-aryl deuterons inside CH_2=CHSi $(OEt)_3$ illustrating the reversible nature of both the C-D addition and the insertion of an olefin into the resultant Ru-D bond, as seen in Figure 5. Corroborating this finding, coupling reactions exhibited a notable ^{13}C KIE (for the ortho carbon), suggesting that the rate-determining step was C-C coupling. A strange case of chemoselectivity manifests itself in this system: coupling occurs only between aryl esters that include electron-withdrawing groups, whereas aryl ketones are able to tolerate both electron-withdrawing and electron-donating groups. According to Murai, this chemoselectivity suggests that the triple-centered σ-complex is not the TS responsible for the rate-determining C-C elimination. Instead, it implies that the alkyl anion moves to the aryl ring, where it may delocalize onto the aryl group. Because the charge may be delocalized on the directing group and returned to the metal core, conjugation between the directing group and the C-H bond undergoing addition may further explain its relevance. Taken together, these results point to a TS for C-C elimination that is similar to the one computed for C-H elimination, as shown (for C-H addition) in equation 22.

A process for dehydrating alkanes

The chemical industry relies on olefins more than any other type of compounds. The capacity to convert alkanes to olefins via dehydrogenation is, hence, very valuable. It was hypothesized that similar species may catalyze dehydrogenation due to the great efficacy of several organometallic hydrogenation catalysts. In 1979, Crabtree noted that this was an important consideration and that $[(Me_2CO)_2IrH_2(PPh_3)_2]^+$ the cycloalkadiene iridium complexes from dehydrogenated cyclopentane and cyclooctane. Dehydrogenation of an alkane to produce free olefin and hydrogen gas requires an acceptor of hydrogen ions to counteract the dehydrogenation enthalpy (ΔH = about +30 kcal/mol). It is believed that the acceptor's mechanical function is to produce an active Ir(I) species. Equation 23 shows that t-Butylethylene (TBE) has the ideal ratio of hydrogen acceptance to weak coordination.



(23)

Despite being mainly driven by the electrophilicity of the cation, it was suggested that the reaction took place via C-H "oxidative" addition. A comparable cycloalkane reaction was later documented by Baudry, Ephritikhine, and Felkin using L_2ReH_7, where the metal center was bonded to the dehydrogenated alkane, and where TBE was used as a hydrogen acceptor. An η^4-trans-1,3-pentadiene complex was produced when this was extended to n-pentane. The remarkable thing is that free 1-alkenes (α-olefins) (122) were produced when the coordinated diene was tried to be removed using trimethyphosphite. Thus, a very selective n-alkane to 1-alkene conversion was accomplished, a reaction that may be very useful if it could be catalytically affected in a high yield. Shortly after, it was shown that cycloalkanes might be catalytically dehydrogenated by means of L_2ReH_7 and L_2IrH_5. Catalyst decomposition reduced the obtained turnover numbers to 70.

6. CONCLUSION

Organometallic C–H bond activation has emerged as an important strategy for transforming relatively inert carbon–hydrogen bonds directly into synthetically valuable functional groups. The development of this field has changed the

conventional perception of C–H bonds from passive structural components of organic molecules to potentially useful reaction sites. As discussed in this paper, transition-metal complexes provide several pathways for accomplishing C–H activation, with electrophilic activation and oxidative addition representing two of the most historically significant mechanistic frameworks. Although these pathways were initially considered fundamentally different, mechanistic investigations have demonstrated substantial relationships between them, emphasizing the complex influence of metal electronic structure, ligands, substrates, and reaction conditions on C–H bond cleavage. Paper 1 @ C-H Activation

The development of platinum-mediated chemistry, particularly the Shilov system, represents a major milestone in selective alkane functionalization. This chemistry demonstrated that even strong C–H bonds in simple hydrocarbons could undergo metal-mediated activation and subsequent conversion into functionalized products under comparatively moderate conditions. The general catalytic sequence involving C–H activation, oxidation, and functionalization also provided an important conceptual framework for the development of later catalytic systems. Nevertheless, the precise mechanism of Pt(II)-mediated C–H activation remains dependent on the catalyst and reaction environment, with both electrophilic and oxidative-addition pathways receiving mechanistic support. Paper 1 @ C-H Activation

The emergence of oxidative-addition chemistry further broadened the scope of organometallic C–H activation. Studies involving ruthenium, rhodium, iridium, platinum, and related transition-metal complexes established that both aromatic and aliphatic C–H bonds could participate in metal-mediated transformations. Particularly important was the demonstration of intermolecular alkane C–H oxidative addition to form stable alkyl–metal hydride species. Such findings established the mechanistic basis for subsequent efforts to incorporate C–H activation into productive catalytic cycles. Paper 1 @ C-H Activation

A major achievement of the field has therefore been the transition from stoichiometric C–H activation to **catalytic C–H functionalization**. Carbonylation reactions demonstrate how activated C–H bonds can be transformed through carbon–carbon bond formation, while transition-metal-catalyzed insertion of olefins and alkynes provides additional routes for constructing more complex molecular frameworks. Directing groups can substantially enhance regioselectivity by facilitating interaction between a particular C–H bond and the catalytic metal centre, thereby enabling site-selective functionalization of otherwise similar C–H bonds. The Ru-catalyzed systems discussed in the paper illustrate the importance of this strategy in developing synthetically useful C–H functionalization reactions. Paper 1 @ C-H Activation

C–H activation also has considerable significance for hydrocarbon conversion. Transition-metal-mediated alkane dehydrogenation demonstrates the possibility of converting relatively unreactive saturated hydrocarbons into more useful olefinic products. The examples involving iridium and rhenium complexes show that organometallic C–H activation can provide pathways toward selective alkane-to-alkene conversion, although catalyst stability, turnover efficiency, thermodynamic constraints, and product selectivity remain important limitations. Paper 1 @ C-H Activation

Overall, organometallic C–H activation provides a powerful conceptual and synthetic platform for achieving more direct transformations of organic molecules. Continued advances in catalyst design, ligand development, mechanistic understanding, regioselectivity, and the use of more abundant metals are expected to improve the efficiency and applicability of these transformations. Future research should particularly focus on catalysts capable of selectively activating specific C–H bonds under mild conditions while minimizing the use of expensive metals, harsh reagents, excessive energy, and stoichiometric oxidants. Such developments could strengthen the role of C–H functionalization in efficient and more sustainable organic synthesis.

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