

## Chemistry of Platinum and Palladium Metal Complexes in Homogeneous and Heterogeneous Catalysis: A Mini Review

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### Abstract

Transition metal complexes of platinum and palladium are most widely used in catalysis. Many synthetic reactions have been carried out with such complexes (used as a catalyst) which have specifically polymer ligands, through hydrosilylation, acetoxylation, hydrogenation, hydro-formylation, oligo-merisation and polymerization. Almost many platinum and palladium catalysts are heterogeneous in nature i.e. the reaction taking place on a solid surface. Now from few years homogeneous catalysts which are completely soluble in the liquid phase reactant, has acknowledged too much attention, yet having small industrial applications, mainly due to the striving of platinum and palladium complexes separation from the catalytic products. More recently a transitional type of platinum and palladium catalysts have been synthesized through attachment of the activated transition metal complexes on the surface of polymer support particularly insoluble which has been established to offer encouraging new collection of catalysts for effective research on synthesis. Many of such complexes will be based on the palladium and platinum metals group. The major objective of this review is to inaugurate the relationship among the reactivity's of homogeneous platinum and palladium complexes and heterogeneous complexes of these metals (those bonded to the surface of metals).

**Keywords:** Complexes; Homogeneous; Heterogeneous; Palladium; Platinum; Catalyst

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## 1. Introduction:

Metal complexes or coordination compounds are the structures made up of a central transition metal atom attached to the surrounding array of anions or molecules (ligands). Transition metal complexes have wide applications in catalysis, materials synthesis, biological systems and photochemistry [1]. Platinum (II) and Palladium (II) metal complexes study was greatly enhanced when it was discovered that they have good catalytic activity and antitumor chemotherapeutic properties. Many efforts have been made to synthesize new Platinum (II) and Palladium (II) complexes which express greater catalytic activity, after knowing the antitumor as well as catalytic activities of *Cis*-ichlorodiammine Platinum (II) [2-4]. The coordination and complexes chemistry of Palladium (II) and Platinum (II) insure a big field as examined in previous literature [5-9] covering the structural and crystallographic data. A remarkable similarity of Platinum (II) and Palladium (II) complexes was found. For example, Palladium (II) and Platinum (II) both are considered as soft metals (class B) which is depicted in their rich chemistry that is not limited to soft bases like phosphorous and sulfur but also for hard ligands e.g. nitrogen and oxygen. They also have similarity in bond lengths and sizes [10], therefore the M-Cl bond present in  $K_2[MCl_4]$  was found to be 2.316 Å for M = Pt and 2.318 Å for M = Pd. The comparatively larger application of Palladium (II) and Platinum (II) complexes in the reaction mechanisms prediction and geometrical isomerism characterization is due to their kinetic inertness [11]. In organic chemistry, Platinum and Palladium are very much being used in the process of catalysis. The fundamental complexes chemistry of palladium and Platinum in the (0), (II) and (IV) oxidation states have been fully explored [12]. Transition metal complexes of Pd (I) found rarely and mostly used as pre catalysts in organic synthesis [13–15]. Substances which can promote a chemical reaction by lowering the activation energy barrier without altering the equilibrium position is termed as a catalyst and reaction which proceed in the presence of catalysts, is called catalysis. The catalytic system may be of heterogeneous in nature or of homogenous. In heterogeneous catalysis, reactants, products, and catalyst are in two -phase systems. In two-phase systems, gaseous or liquid reactants and products and a solid catalyst material--typically metal or metal oxides are often dispersed on ceramic supports. In homogeneous catalysis, reactants, products, and catalyst are in single-phase systems, typically a transition ion metal complexes are dissolved in an organic solvent.

## 2. Comparison between Heterogeneous and Homogeneous Catalysts:

The well-known relative merits of heterogeneous and homogeneous catalysts of transition metals complexes of Palladium and Platinum are only stated here. Homogeneous catalysts have more effective active sites it means that all of the transition metals atom available as the catalyst, furthermore the electronic and steric environment of the metals atom can be varied widely, at least in principle. The main drawbacks of using homogeneous catalyst are non-recovery, poor separation of reaction products and easily decomposition of catalysts as compared to heterogeneous catalysts. Therefore the reaction conditions like temperature must be well controlled and if poisonous by-products are formed they can be deactivated. Corrosion of reactors is also possible by the use of metal complexes. Simply this can be both expensive as well as complex. The disadvantages can be avoided and advantages could be retained if the homogeneous catalysts are either chemically bonded to it or adsorbed on to surface of solid support.

Homogeneous Catalysts when compared with heterogeneous catalysts, they

- more reactive at lower temperatures and pressures

- more active per metal center
- more selective in products formed
- easily studied and modified
- Operate at 50°-1500~ and 50-500 psi to produce  $kI_2/CO$
- Better heat transfer is allowed
- Use discrete, well-defined catalytic species that arc more

Heterogeneous Catalysts when compared with homogeneous catalysts, they

- Are thermally more stable, because they
  - Allow higher reaction rates at higher temperatures
  - Have longer catalyst lifetime
  - Regenerate the catalyst in situ
- Produce reactants and products that are more readily separated from catalyst
- Operate at 200~300 °C and 500-1500 psi to produce  $H_2/CO$  [16].

### 3. Platinum Based Homogeneous Catalysis:

Randall LT et al (1992) explored relationship between the reactivity's of alkyl groups attached to surface of Platinum (II) metal (heterogeneous) and those attached to platinum in homogeneous platinum (II) complexes. That research was done using the following argument: if the observed catalytic reactions for alkyls group in homogeneous metal complexes comparable those heterogeneous (on the surface of Pt), we should be able to account for the heterogeneous processes in terms of highly localized or single center chemistry. Otherwise, if there is no relationship between homo and hetero alkyl reactions we might follow the proposal that bulk transition metals possess distinctive reactivity. The relative rates of carbon-hydrogen (C-H) bonds activation of alkyl groups in homogeneous complexes positioned at **a,8,6,y** and **c** to platinum metal was shown: **0 > 6 > y = E >> a** (yet not observed) [17-20]. They applied the following scheme to give analogous relative rates of C-H bonds activation of alkyl groups for surface alkyl Platinum. A number of platinum complexes were hydrogenated as shown in equation 1 and investigated the value of deuterium in the product cyclo-octanes. From the deuterium value, we observed the relative rates of carbon hydrogen (C-H) bond activation of the surface metal alkyls: **a > B > 6 > y = t**. The relative rates of reactions in solution and on the surface were similar except for carbon hydrogen (C-H) bond activation: the least facile process in solution is activation that is the most facile process on the surface. Perhaps the utmost probable reason of this difference is that facile a activation on platinum metal required at least two metal centers [21].

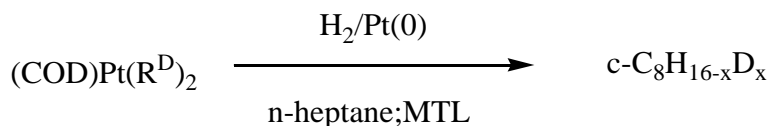


Fig 1: Reaction Scheme of C-H bond activation from deuterium contents

Table 1: Relative rates of C-H bond activation from deuterium contents

R <sup>D</sup>	X
CD <sub>3</sub>	0.71
CD <sub>2</sub> CH <sub>3</sub>	0.68
CH <sub>2</sub> CD <sub>3</sub>	0.15
CH <sub>2</sub> CH <sub>2</sub> CD <sub>3</sub>	0.05
CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CD <sub>3</sub>	0.02

#### 4. Palladium Based Homogeneous Catalysis:

The catalytic activity of two newly synthesized and characterized Pd complexes was monitored for the aldol reactions of aldehydes with methyl isocyano-acetate. Each and every palladium atom was coordinately attached to S-C-S-type ligands and the two pincer units were connected by a chiral spacer. But substantial enantio-selectivity and diastereo-selectivity was not found by the catalytic aldol reactions of methyl isocyano-acetate with aldehydes even they preceded fastly. Homologous mononuclear Palladium complexes when compared with the bimetallic compounds no difference was found and hence it was concluded that metal centers have no compliance. On silica-support two catalysts were synthesized with a bimetallic compound indicated catalytic activity along a little enantio-selectivity [22]. N-heterocyclic carbene (N-H-C) ligands have become important ligands for the synthesis of metal complexes with new catalytic applications. Mainly because of their applications in carbon-carbon bond formation reactions i.e. novel palladium-N-H-C complexes, and a large number of review articles have been published exploring their catalytic chemistry. Their main focus was on following points: Design of reusable Pd-N-H-C complexes, Latest advancement in the use of Pd- N-H-C complexes in homogenous catalysis and many more suitable applications of Pd-N-H-C complexes [23].

#### 5. Aryl-Heteroatom Coupling: C-O and C-X Bond Formation:

The catalytic cycle used for chelating controlled position selective aryl oxidation reactions is thought to complete via the formation of palladacycle which is then followed by the oxidation of palladium to Pd(IV) and then later reductive carbon-heteroatom bond formation[24].

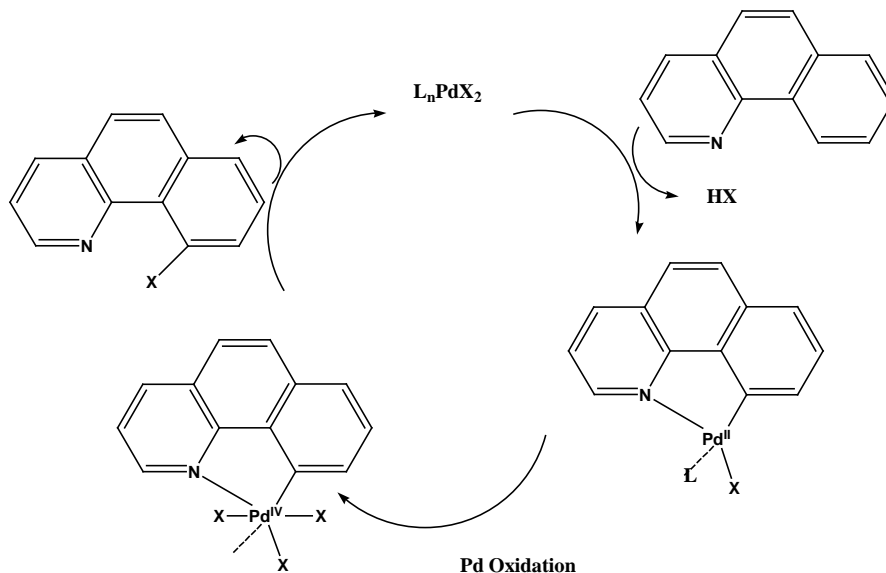


Figure 2: Catalytic cycle for the palladium (IV) catalyzed aryl oxidation

## 6. Platinum and palladium catalysis in medicinal applications:

Significant anticancer entities like cisplatin, carboplatin, and oxaliplatin were synthesized by clinical, Chemical and pharmacological-research on anticancer coordination metals complexes. After the invention of cisplatin, the advancement of similar complexes has been a realistic chore. Literature revealed that the varieties of platinum complexes having antitumor activity were not limited to the structural similarities of cisplatin. The conventional structure activity rules have been broken: *trans*-platinum complexes, active platinum complexes without NH groups, cationic complexes, multinuclear complexes and numerous classes of palladium (II) complexes have developed. To develop and opportune anticancer drugs which show prime efficiency against human tumors was the primary target of most research groups. Many research articles have been published giving an up to date summary of the anticancer chemistry of complexes of platinum and palladium and the new strategies applied for the synthesis of new platinum and palladium antitumor products [25].

## 7. Heterogeneous Catalysis:

In heterogeneous catalysis, reactants, products, and catalyst are in two phase systems. In two phase systems, gaseous or liquid reactants and products and a solid catalyst material typically a metal or metal oxide are often dispersed on ceramic supports.

### 7.1 Platinum Based Heterogeneous Catalysis:

Randall *et al* (1992) did a splendid job and discovered heterogeneous addition of hydrogen in (diolefin) dialkyl complexes of platinum (II). They showed that if there is possibility to produce structurally well-defined surface alkyls under organo-synthetic conditions by using a combination of catalysis and organometallic chemistry. Then these reactions suggest new techniques of reviewing surface alkyls by applying standard physical organic probes: stereochemistry, isotopic labeling and rate-structure profiles [26].

### 7.2 Palladium Based Heterogeneous Catalysis:

For catalysis, Palladium is the most extensively used metal in organic chemistry. The fundamental complexes chemistry of Pd in the (0), (II) and (IV) oxidation states have been fully explored [27]. Transition metal complexes of Pd (I) found rarely and mostly used as pre catalysts in organic synthesis [28–30]. The organometallic chemistry of Pd (III) found in its initial stages when compared with Pd (0), (II) and (IV). Limited accurate complexes of Pd(III) are well-known. We review the organometallic chemistry of well-defined, isolated Pd(III) complexes, as well as organometallic chemistry in which the potential role of Pd(III) intermediates is currently more hypothetical [31].

### 8. Pd-Catalyzed Carbon-Carbon Coupling Processes:

The Suzuki, Heck, Negishi, Sonogashira, Corriu-Kumada, Stille, Tsuji-Trost, Ullmann and Hiyama reactions are good examples of Palladium catalyzed Carbon-Carbon coupling reactions as shown in Fig 3. It is particularly easy to carry out the earlier two reactions because they have no need to include the initial synthesis of organo-element compounds, whereas the next four reactions require the initial preparation. The Suzuki reaction was considered utmost suitable because these synthesized compounds were nontoxic as compare to other organometallic compounds e.g. the organo-tins in this second group. The Heck reaction was also frequently applicable and it has also been explored by PdNPs catalysis. In this reaction, PdNPs were all the most possibly involved beginning from molecular Palladium catalysts because of high reaction temperatures (need  $>100\text{ }^{\circ}\text{C}$ ). Indeed, the molecular Palladium precursors were establish to create PdNPs which are the bases of catalytically active species in numerous cases, but these in situ produced PdNPs have habitually not been reflected as possible intermediate [32].

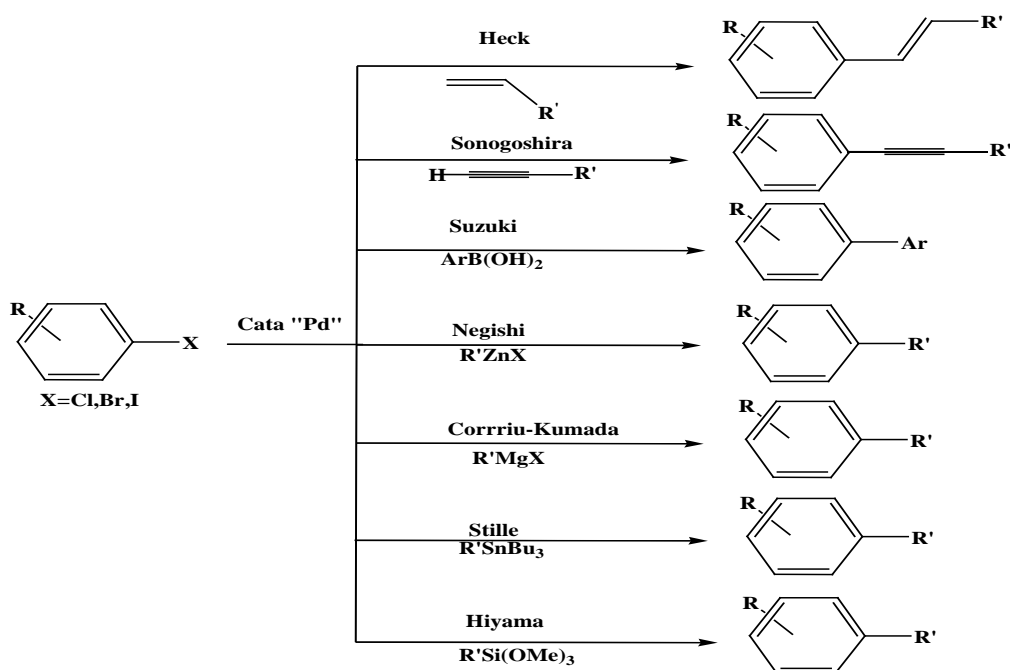


Figure 3: Catalysis by Pd for C-C Bond Formation

The immobilization of homogeneous catalysts onto polymeric inorganic or organic [33-39] support, provides the benefits of easy catalyst recovery, product separation, inhibiting the loss of metal and reusing property. Pd-catalyzed cross-coupling reactions were the main organic transformations for the production of Carbon-Carbon bonds [40-44]. Therefore, different cross-coupling reactions have been investigated as mentioned above in figure 3. The cross-coupling reactions of vinyl, aryl, benzyl, allyl halides, triflates and acetates with alkenes recognized as Heck reactions [45-47]. The terminal alkynes react with aryl halides termed as Sonogashira-Hagihara reaction [48-50] and important illustration of carbon-carbon bond formation is the reaction of organo-boron compounds with pseudo halides or organic halides famous as Suzuki-Miyaura reaction [51, 52]. Mostly the coupling reactions were accomplished using palladium catalysts containing ligands i.e. amines, dibenzylidene acetone, phosphine, carbene etc. [40]. Substitution of phosphine ligands in palladium-catalyzed coupling reaction was achieved with nitrogen-chelating ligands that were inexpensive and stable. Poly-nitrogenated compounds permit functional-ligands which could make coordination with palladium [47]. Within these compounds, because of beginning material availability and flexibility to facilitate chemical amendment imidazolium types are of great interest. Until now, functional polymer comprising imidazolium groups and imidazolium ligands immobilized onto silica supports [53, 54] have been added in Pd-catalyzed coupling reactions. Imidazolium type ligands adsorbed onto silica support permit greater catalytic activity. Moreover, literature review provide sufficient information about carbon-carbon coupling reactions catalysed through amended mesoporous (molecular sieves based) catalysts, i.e. palladium catalysts settled on S-B-A-15 type molecular sieves improved with amines donor group [55], mesoporous organo-silica consisting of a carbon palladacycle complex [56], mesoporous molecular sieve substituted with various Nitrogenous groups [57], palladium catalyst settled on silica supports [58], and Pd-nanoparticles adsorbed in sponge like porous silica [59] etc. By taking consideration about demands and applications of heterogeneous silica-based palladium catalysts, the other requirement was to establish and design active, stable, reusable and reproducible catalysts. In extension of past research on heterogeneous polymer support palladium catalysts [60] and polymers grafted silica palladium catalysts [61, 62] the production and applications of poly(N-vinyl imidazole) grafted-silica palladium complex was reported. That heterogeneous Palladium catalyst was efficient for Sonogashira, Heck and Suzuki reactions using different substrates in addition to chloro-arenes as well as reproducible and beneficial to environment. The catalyst was successfully used with a variety of aryl halides in Heck, Sonogashira and Suzuki coupling reactions. Distinct aryl halides showed good reactivity including readily obtained chloro-arenes to create the relevant products in good to excellent amount produced. XRD and TEM study of catalyst exposed small particles size in nano scale and high metal dispersal. Heck, Sonogashira and Suzuki coupling reactions were explained for high competence of catalyst, good dispersion into the reaction system, easy purification of product, better yield, short reactions time and air protected reactions [63]. Furthermore, literature reviews explore the synthesis and applications of palladium (II) supported hydro-talcites (Pd-HT)[64, 65]. Pd-HT also showed well functionality and reusability for Heck reaction between olefins and aryl halide to make carbon-carbon coupling products with optimum yield [67]. In functionalized and activated aromatics, C-H bonds will be attacked by Pd-salts such as aceto aniline to make palladium carbon bond that afterward experience insertion of alkene [68]. Palladium catalysis of carbon-carbon bond formation is precisely studied from the angles of nano particle whether these are heterogeneous or homogeneous pre-catalysts

and are deliberately produced or preformed from a Palladium derivatives i.e. Pd(OAc)<sub>2</sub>. The Heck coupling of halogenoarenes with olefins is the most studied reaction that mostly proceeds at high temperature (120-160 °C). Species generated from preformed Pd-nanoparticles can also catalyze other carbon-carbon coupling reactions such as Sonogashira, Suzuki, Stille, Hiyama, Tsuji-Trost, Ullmann, Corriu-Kumada, and Negishi. Leaching of active Palladium atoms from the Pd-nanoparticles for catalysis of these reactions, may also supply a practicable molecular mechanistic plan of action. Thus, Pd-nanoparticles acts as precursor of catalytically active Palladium specie i.e. the Pd-nanoparticles are pre-catalysts of carbon-carbon coupling reactions [69]. Platinum and palladium based reactions catalyzed by polymer-supported transition metal complexes of said metals are summarized in Table 2.

Table 2: Reactions Catalysed by Polymer-Supported Transition Metal Complexes

<b>Metal Complexes</b>	<b>Polymers</b>	<b>Substrates</b>	<b>References</b>
<b>Hydrogenation</b>			
PtCl <sub>2</sub> PdCl <sub>2</sub>	phosphenated polystyrene -divinyl benzene	soybean methyl ester	70
K <sub>2</sub> PdCl <sub>4</sub>	Amberlyst A27	cyclohexene styrene	71
<b>Hydrosilylation</b>			
RhC <sub>3</sub> or H <sub>2</sub> PtCl <sub>4</sub>	cross-linked polystyrene -divinyl benzene substituted with -CH <sub>2</sub> CN polymethacrylate with ester group -CH <sub>2</sub> PPh <sub>2</sub> , or -CH <sub>2</sub> NMe <sub>2</sub> -OC <sub>6</sub> H <sub>2</sub> PPh <sub>2</sub> or -O(CH <sub>2</sub> ) <sub>2</sub> CN or -O(CH <sub>2</sub> ) <sub>3</sub> PPh <sub>3</sub> or -O(CH <sub>2</sub> ) <sub>2</sub> NMe <sub>2</sub> Amberlyst A21 allyl chloride-divinylbenzene copolymer with - CH <sub>2</sub> PPh <sub>2</sub> functional group	hex-I-ene hept-I-ene with HSi(OEt) <sub>3</sub> or HSiCl <sub>3</sub> or HSiEt <sub>3</sub>	72
<b>Acetoxylation</b>			
PdCl <sub>2</sub>	phosphenated silica	ethylene propylene isobutene	73

## 9. Conclusion:

This review reveals that research interest in transition metal complexes of platinum and palladium in catalysis has increased within short time. Heterogeneous catalytic system was mainly used for synthesis. But now scientists are stepping toward homogeneous systems which have many advantages over heterogeneous system. The technological hurdles in using homogeneous catalysts have undoubtedly been the main reason in initiating this work. It is to be expected that the benefits that homogeneous catalysts sometimes have to give over their heterogeneous counter parts can be understood by putting the catalyst on a polymer support. As the working of these systems has only started to be investigated, it continues at an increasing rate undoubtedly.



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