

Transition Metal Complexes: A Review Of Design, Reactivity, And Industrial Applications

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Transition metal complexes are a mainstay of modern inorganic and organometallic chemistry, owing to their extraordinary structural diversity, tunable properties, and broad applications. Their unique electronic structures and variable oxidation states allow them to participate in a wide range of chemical reactions, making them critical for catalysis, materials science, and industrial chemistry. These complexes are designed by rationally choosing the metal centers and ligand frameworks to tune the electronic and steric environment to control reactivity and stability. Advanced ligand systems such as chelating, pincer and redox-active ligands have greatly extended the scope of catalytic performance and selectivity. Oxidative addition, reductive elimination, ligand substitution, migratory insertion, etc. are important mechanistic steps that dictate the reactivity of transition metal complexes and are the basis of catalytic cycles. In-depth mechanistic understanding, such as the inner- and outer-sphere electron transfer pathways and metal-ligand cooperative interactions, has allowed the rational design of effective catalytic systems. Furthermore, the activation of small molecules such as hydrogen, oxygen, carbon monoxide, and nitrogen under mild conditions demonstrates their pivotal role in energy conversion and chemical synthesis. Transition metal complexes find wide applications in industrial processes such as petrochemical processing, polymerization, environmental remediation and pharmaceutical synthesis. Platinum, palladium and rhodium are metals that catalyze important transformations such as hydrogenation and carbon-carbon coupling. The production of polymers can be controlled using Ziegler-Natta and metallocene catalysts. Moreover, their involvement in pollutant degradation and CO₂ reduction promotes sustainable practices and their use in drug synthesis increases efficiency and decreases waste.

Future developments focus on the use of earth-abundant metals, integration of machine learning for catalyst design, and bio-inspired systems for green chemistry. Continued advances in ligand engineering and mechanistic understanding will further expand their applications. Overall, transition metal complexes remain central to chemical innovation, offering sustainable solutions for current and emerging industrial challenges.

Keywords: Transition metal complexes, Ziegler-Natta, green chemistry, Oxidative addition, pharmaceutical synthesis.

1. Introduction

Transition metal complexes are one of the cornerstones of modern inorganic and organometallic chemistry. They are defined as complexes formed between central metal atoms and a variety of ligands (Cotton et al., 1999, Crabtree, R. H. 2009, Hartwig, 2010). The unique versatility of the transition metals arises from their electronic configurations and variable oxidation states, such that these complexes can participate in a range of chemical

transformations (Crabtree, R. H. 2009; Miessler et al., 2011). They are of importance from fundamental research, to practical applications, especially in catalysis, materials science and industrial chemistry (Bell, 2003; Nicolaou et al., 2005). Transition metal complexes have become the most important players in synthetic methodologies and sustainable industrial processes, because of their tunable properties through rational ligand design and choice of metal (van Koten & Milstein, 2013).

Transition metal complexes are designed by the deliberate choice of metal centers and ligand frameworks that tune the electronic and steric environment around the metal (Elschenbroich, 2006). Early transition metals are generally characterized by high oxidation states and different reactivity patterns than late transition metals commonly exploited for redox catalysis (Shriver & Atkins, 2010). The architecture of the ligand is important in stabilizing the metal centers and directing the reactivity. Ligands can be neutral, anionic and cationic species with donor atoms such as nitrogen, phosphorus, oxygen and sulfur (Housecroft & Sharpe, 2008). Advances in ligand design, including pincer and redox-active ligands, have broadened the range of electronic properties that can be achieved, allowing for fine-tuning of catalytic activity and selectivity (van Koten & Milstein, 2013; Gunanathan & Milstein, 2013).

The basic mechanistic steps like oxidative addition, reductive elimination, ligand substitution and migratory insertion govern the reactivity patterns of transition metal complexes (Hartwig, 2008). These processes are the basis for catalytic cycles that are at the heart of many synthetic transformations (Beller & Bolm, 2004). A detailed mechanistic understanding involving inner- and outer-sphere electron transfer pathways, and cooperative metal–ligand interactions, has opened up avenues for the rational design of more efficient and selective catalysts (Taube, 1984). The activation of small molecules such as hydrogen, oxygen, carbon monoxide, and nitrogen under mild conditions highlights the important role of transition metal complexes in energy conversion and chemical feedstock transformations (Schrock, 2008).

Transition metal complexes have been used in a wide range of industrial applications for their catalytic properties (Thomas & Thomas, 1997). In the petrochemical industry, platinum, palladium and rhodium complexes are the catalysts for important reactions like hydrogenation, hydroformylation and carbon-carbon coupling (Cornils & Herrmann, 2002). Polymerization catalysts, e.g. Ziegler–Natta and metallocene systems, allow the synthesis of polymers with controlled architectures (Kaminsky, 1998). Transition metal complexes are applied to environmental applications, e.g. pollutant degradation (Aresta & Dibenedetto, 2007) and carbon dioxide reduction. Moreover, metal-catalyzed cross-coupling reactions have revolutionized pharmaceutical synthesis by improving efficiency and minimizing waste (Nicolaou et al., 2005).

Future disruptive advances in the field are ripe to be achieved through the use of earth-abundant metals in place of precious metals, the use of machine learning and computational tools for catalyst design, and the development of bio-inspired catalytic systems. Continued advances in ligand design and mechanistic understanding will further extend the role of transition metal complexes in both academia and industry, enabling sustainable and efficient chemical processes.

This review offers a comprehensive overview of the design principles, mechanistic insights and industrial applications of transition metal complexes, emphasizing recent progress and future directions that underscore their continuing importance in modern chemistry.

2. Design of Transition Metal Complexes

The design of transition metal complexes is fundamentally based on the judicious choice of the metal centre and the ligand framework which have a profound effect on the properties and reactivity of the complex. The choice of transition metals, mainly from the d-block groups 4-11, is motivated by the availability of oxidation states and coordination flexibility (Hartwig, 2010). In general, redox catalysis involves late transition metals, which are easily oxidized and reduced, while early transition metals are more oxidized and have different reactivity patterns (Hartwig, 2010).

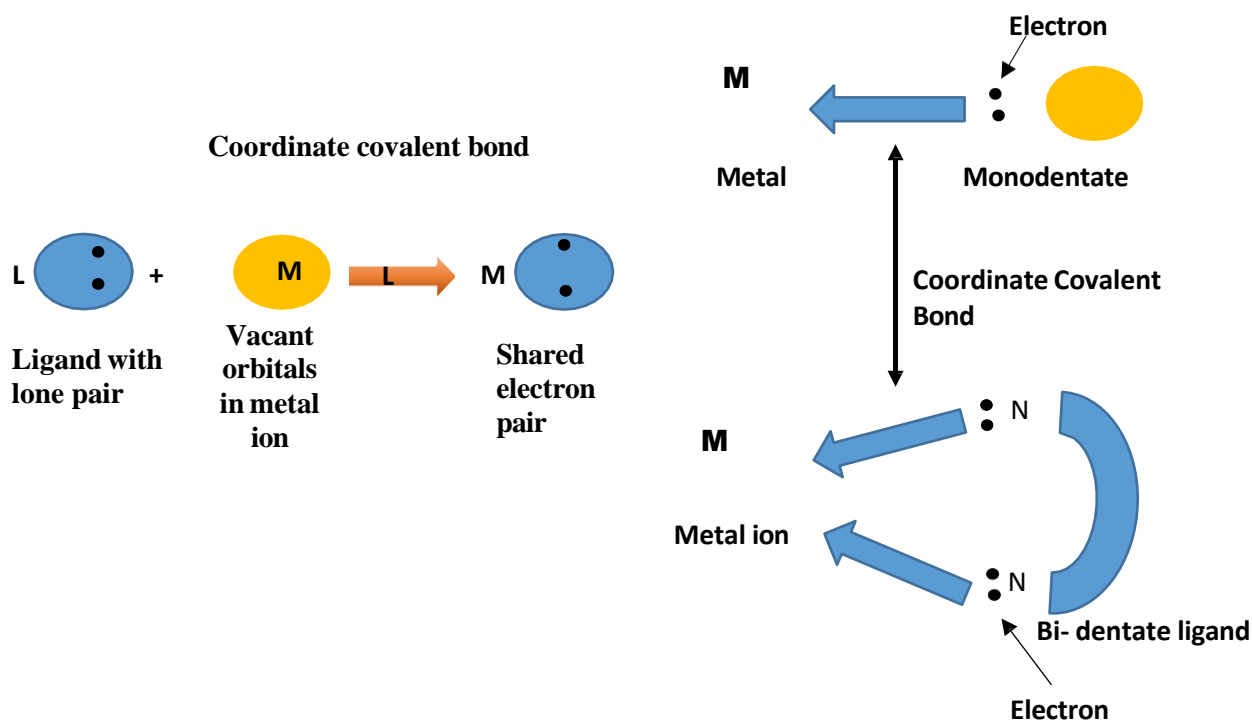


Fig 1: Schematic representation of the mechanism behind the formation of metal complexes

The diagram shows the formation of transition metal complexes by coordinate (dative) covalent bonding between a metal ion and ligands. The ligand has a lone pair of electrons. The metal ion has empty orbitals that can accept electrons. This is a coordinate covalent bond where both electrons are donated by the ligand. This bonding is the basis of coordination chemistry and is the basis of the structure of all transition metal complexes (Fig 1). The figure also differentiates between the different types of ligands based on their binding ability. Ligands with one donor atom and forming only one bond to the metal center are called monodentate

ligands. Bidentate ligands, on the other hand, have two donor atoms and may bind to the same metal ion at two coordination sites. This often results in the formation of a chelate ring, which increases the complex's stability. In the diagram, the donor atom is nitrogen, but it could also be oxygen or sulfur or any other heteroatom with lone pairs to donate. In general, the diagram illustrates the role of ligands in donating electron pairs to metal ions in the formation, structure and stability of coordination complexes. Ligand architecture is important for the stabilization of the metal center and for tuning its electronic and steric environment (Elschenbroich, 2006). Ligands are often classified as neutral, anionic or cationic and donor atoms can be nitrogen, phosphorus, oxygen and sulfur, providing a variety of bonding interactions (Housecroft & Sharpe, 2008). Multidentate ligands give rise to the chelate effect, which increases the stability of complexes (Hartwig, 2010). Recent advances in ligand design include pincer ligands and redox-active ligands which allow for precise control over electronic properties and catalytic behavior (van Koten & Milstein, 2013; Gunanathan & Milstein, 2013). Ligand modification tunes the electronic and steric parameters that in turn tune the catalytic activity and selectivity. Electronic tuning changes the electron density at the metal center and is a factor in the reaction pathways. Steric bulk enforces the geometry and prevents unwanted side reactions (Hartwig, 2008).

2.1 Metal Selection

Metals of the d-block, particularly groups 4–11, are widely used because of their accessible range of oxidation states and coordination modes (Hartwig, 2010). These metals are known to have multiple accessible oxidation states suitable for redox processes and catalytic cycles. Early transition metals (groups 4– Nicolaou et al., 2005) generally form complexes in higher oxidation states as a result of their electronic configuration. This results in a high electrophilic character and strong metal-ligand bonds, rendering them suitable for polymerization and oxidation catalysis.

This is due to their electron configuration and relatively low effective nuclear charge which favors the loss of multiple electrons. Therefore, early transition metals readily engage in high electrophilic reactions and form strong metal-ligand bonds, making them suitable for polymerization and oxidation catalysis. Widely used are the metals of the d-block, especially groups 4 to 11 because of their variable oxidation states and coordination abilities. These metals have a variety of accessible oxidation states and can thus participate in redox processes and catalytic cycles. The early transition metals (groups 4-6) have electronic configurations that favor complex formation in higher oxidation states. This gives a strong electrophilic character and a robust metal-ligand bonding and, therefore, makes them suitable for polymerization and oxidation catalysis (Kaminsky, 1998). The ability of late transition metals to stabilize lower oxidation states and partake in oxidative addition and reductive elimination steps is central to their widespread use in homogeneous catalysis.

2.2 Ligand Architecture

Ligands form the basic components of coordination complexes and their structure greatly influences the stability, reactivity and overall performance of the complexes (Housecroft & Sharpe, 2008). Ligands can be neutral, anionic or cationic and typically bind to metal centers via donor atoms such as nitrogen, phosphorus, oxygen and sulfur, which donate lone pairs of

electrons for coordination. The nature of these donor atoms is of great importance for the electronic environment of the metal and consequently for its chemical behavior and catalytic properties. Chelating ligands are one of the most important contributors to the stability of complexes. They bind through several donor sites to form ring-like structures. The chelate effect increases stability by decreasing the probability of ligand dissociation and increasing thermodynamic favorability (Hartwig, 2010). In recent years, the search for advanced ligand systems has broadened the scope and utility of transition metal complexes. Pincer ligands are well known for their stiff tridentate structures that provide outstanding structural stability and the possibility of fine-tuning the coordination geometry and electronic properties of the metal center. Moreover, redox-active ligands are a powerful class of ligands that participate in the electron transfer processes instead of being passive spectators. These ligands provide the ability to fine-tune oxidation states and stabilize reactive intermediates and therefore enable catalytic cycles (van Koten & Milstein, 2013; Gunanathan & Milstein, 2013). Thus, fine design and modification of ligand architecture have now become indispensable strategies for optimization of catalytic efficiency, selectivity and durability in applications of modern coordination chemistry.

2.3 Electronic and Steric Tuning

One major strategy to control the behavior and performance of coordination complexes is electronic and steric tuning of ligands. Ligands can be electronically tuned to control the electron density at the metal Centre and this will have a direct impact on reactivity, stability and catalytic efficiency (Hartwig, 2010). Ligands with electron donating groups increase the electron density at the metal often making it more able to take part in bond activation processes. Electron withdrawing groups decrease the electron density and thus affect oxidation states and reaction pathways. These electronic modifications provide chemists with the tools to customize catalysts for specific transformations and to enhance their overall performance. Steric factors are also important in determining the properties of coordination complexes, besides electronic effects. Large substituents on the ligand framework generate a well-defined three-dimensional environment around the metal center. This steric hindrance can impose specific coordination geometries, stabilize reactive intermediates and control the accessibility of substrates to the metal site (Hartwig, 2008). Steric effects are useful in suppressing side reactions by limiting the approach of undesired reactants and increasing the selectivity in catalytic processes. Electronic and steric tuning, jointly, represent a powerful and versatile strategy for the design of advanced metal complexes with optimized performance. Ligand modification can be considered to provide more control over catalytic activity, selectivity and durability. Thus, these strategies are widely applied for the development of efficient catalysts for industrial, environmental and synthetic applications, making them indispensable tools of modern coordination and organometallic chemistry.

3. Reactivity of Transition Metal Complexes

The reactivity of transition metal complexes is largely determined by their ability to undergo fundamental organometallic processes such as oxidative addition, reductive elimination, ligand substitution, and migratory insertion. Oxidative addition involves the increase in oxidation state and coordination number of the metal center, enabling the activation of strong

chemical bonds. In contrast, reductive elimination leads to the formation of new bonds between ligands while reducing the metal's oxidation state

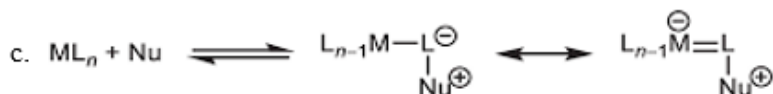
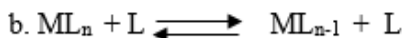
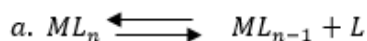


Fig 2: Typical reactivity of transition metal complexes a Dissociation, b ligand substitution reactions and c reactions at the ligand of transition metal complexes (Nu: nucleophile)

The diagram illustrates fundamental processes involved in ligand substitution reactions of transition metal complexes. In the first step, ligand dissociation ($ML_n \rightleftharpoons ML_{n-1} + L$), a coordinated ligand detaches from the metal center, generating a complex with a lower coordination number and creating a vacant site for incoming species. The second step represents ligand substitution ($ML_n + L' \rightleftharpoons ML_{n-1}L' + L$), where an incoming ligand replaces an existing one, resulting in the exchange of ligands around the metal center. Depending on whether ligand loss or ligand addition occurs first, the process can proceed via different pathways. The third part presents a mechanistic pathway based on the nucleophilic attack, in which a nucleophile interacts with the metal complex to form a transient intermediate. This intermediate rearranges, often with changes in bonding and charge distribution, and eventually displaces ligands. Taken together, these steps are illustrative of the dynamic nature of coordination complexes and the mechanisms controlling their reactivity.

Ligand substitution reactions enable the substitution of coordinated ligands, which alters the stability and reactivity of the complex. Another important step is migratory insertion, in which a ligand migrates into a metal–ligand bond, often facilitating chain growth or bond formation in catalytic cycles (Beller & Bolm, 2004). Together, these processes play a key role in controlling the catalytic behavior and mechanistic pathways of transition metal complexes in a range of chemical transformations.

3.1 Catalytic Cycles

Many catalytic reactions of transition metal complexes proceed via cyclic mechanisms, where the metal center alternates between different oxidation states. Redox changes are important for allowing important reaction steps such as bond activation, formation and rearrangement. During the catalytic cycle, the metal alternates between higher and lower oxidation states, allowing oxidative addition and reductive elimination to occur in a controlled manner. This dynamic behavior allows the catalyst to be used again and again without being consumed. To increase reaction efficiency, selectivity and stability a thorough understanding of these catalytic cycles is necessary. By unraveling the relationship between oxidation state variation and reactivity, rational design of more active catalysts with improved performances for industrial, environmental and synthetic applications is possible.

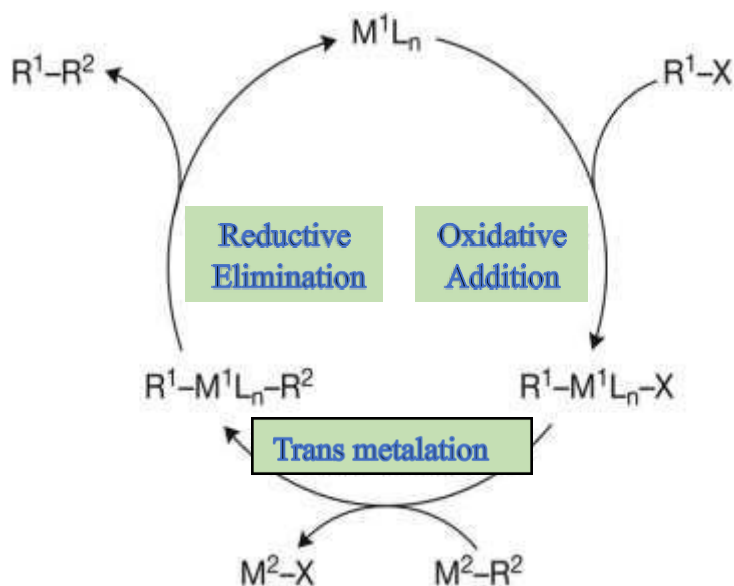


Fig. 3: Generic catalytic cycle of a transition-metal-catalyzed cross-coupling reaction

This diagram represents a typical catalytic cycle of transition metal-catalyzed cross-coupling reactions, involving three key steps: oxidative addition, trans metalation, and reductive elimination. The cycle begins with the metal complex (M^1L_n) in a lower oxidation state. In the first step, oxidative addition, an organic substrate (R^1-X) reacts with the metal center, forming a new complex ($R^1-M^1L_n-X$). During this step, the metal increases its oxidation state and coordination number as it forms bonds with both R^1 and X . Next is trans metalation, where another metal species (M^2-R^2) transfers the R^2 group to the central metal complex, replacing X . This results in the formation of a di-organometallic intermediate ($R^1-M^1L_n-R^2$), while the by-product (M^2-X) is released. Finally, reductive elimination occurs, where the two organic groups (R^1 and R^2) combine to form a new carbon-carbon bond (R^1-R^2). This step regenerates the original metal catalyst (M^1L_n) in its lower oxidation state, allowing the catalytic cycle to continue.

Overall, this cycle demonstrates how transition metal catalysts facilitate bond formation efficiently by cycling between oxidation states and coordinating different reactants in a controlled sequence of steps.

3.2 Mechanistic Pathways

Detailed mechanistic studies on transition metal complexes provide deep insights into the pathways that control their reactivity and catalytic activity. Such studies often uncover mechanisms such as inner-sphere and outer-sphere electron transfer processes. In inner-sphere mechanisms, a ligand is present that bridges between the metal center and substrate and promotes direct electron transfer. In outer-sphere mechanisms, electron transfer is mediated in the absence of direct bonding interactions. Furthermore, ligand-assisted transformations are highly significant where ligands actively participate in bond activation or stabilization of

intermediates. Cooperative effects between the metal center and ligand framework further enhance reactivity, where the synergistic action of both components results in reduced activation barriers and increased efficiency (van Koten & Milstein, 2013; Gunanathan & Milstein, 2013). Such mechanistic insight is indispensable for the rational design of advanced catalytic systems with enhanced selectivity, activity and functional performance.

3.3 Activation of Small Molecules

Transition metal complexes are important in the activation of small molecules such as H₂, O₂, CO and N₂ under relatively mild conditions. The molecules themselves are stable, due to strong covalent bonds and high bond dissociation energies. In the absence of a catalyst these molecules are relatively unreactive. But when coordinated to a transition metal center, their bonds can be significantly weakened so that chemical transformations that would otherwise be difficult to achieve can be attained. The interaction involves the processes of oxidative addition, pi-back bonding and electron transfer between the metal and the substrate. This allows the cleavage and formation of bonds. Oxidative addition allows the metal to insert into strong bonds like H-H or C-X, increasing the metal's oxidation state and allowing for further reactivity. pi-Back bonding, which is common in such molecules as CO and N₂, is where electron density is donated from the metal into the antibonding orbitals of the ligand, thereby weakening the internal bonds of the molecule. Furthermore, electron transfer processes stabilize reactive intermediates and assist in catalytic turnover. They are central to many industrially important reactions such as hydrogenation, oxidation, carbonylation and nitrogen fixation. The activation of small molecules is especially important for energy-related applications, including fuel production and storage, and for the synthesis of valuable chemical feedstocks. Better understanding of these processes allows the rational design of efficient and sustainable catalytic systems. Such development contributes to the realization of environmentally friendly chemical processes and the support of the wider goals of green chemistry and sustainable industrial development.

4. Industrial Applications

Transition metal complexes with high catalytic efficiency, selectivity and versatility are important in many industrial processes. Their capacity to catalyze a range of chemical transformations under mild conditions makes them indispensable for large scale production. Such complexes are extensively used in processes such as hydrogenation, hydroformylation, polymerization and oxidation reactions which are essential for the production of fuels, plastics, pharmaceuticals and fine chemicals. They have tunable electronic and steric properties which help in adjusting reaction pathways to get higher yields and less by-products (Crabtree, R. H. (2009)). Moreover, transition metal catalysts contribute to the creation of more sustainable and energy-efficient industrial processes by reducing energy requirements and minimizing waste generation. Thus, they are still crucial for the advancement of modern chemical industries and the development of greener technologies.

4.1 Catalysis in Petrochemical Industry

Platinum, palladium and rhodium transition metal complexes are of pivotal importance in catalysis in the petrochemical industry due to their exceptional activity and selectivity. These

metal complexes are widely applied in important processes such as hydrogenation, hydroformylation, and carbon-carbon coupling reactions, which are the foundation of refining and synthesis of fuels and value-added chemicals. Hydrogenation reactions are important in the conversion of unsaturated hydrocarbons to saturated products and in the improvement of stability and quality of fuels. Hydroformylation is a process that turns alkenes into aldehydes, important intermediates for the production of alcohols, plastics and detergents. Palladium-catalyzed carbon-carbon coupling reactions are also widely used in the construction of complex molecular architectures in fine chemicals and pharmaceuticals. The efficiency and tunability of these metal complexes make them essential in modern petrochemical processing and industrial synthesis.

4.2 Polymerization Catalysts

Polymerization catalysts are important for the controlled synthesis of polymers with desired structural and physical properties. The most important among them are Ziegler-Natta catalysts and metallocene catalysts which are usually based on transition metals like titanium, zirconium and other group metals. Ziegler-Natta catalysts are widely used for the production of polyethylene and polypropylene, with the ability to control polymer stereochemistry and molecular weight (Kaminsky, 1998). Even higher precision for the control of polymer architecture, such as tacticity and chain distribution, is offered by metallocene catalysts with well-defined single-site structures. Using these catalysts, polymers with certain properties such as strength, flexibility and thermal stability can be synthesized. They are therefore important in the production of a wide range of materials used in packaging, automotive components, textiles and advanced engineering applications.

4.3 Environmental Applications

Transition metal complexes are of great importance in environmental applications, such as the efficient degradation of pollutants and the reduction of carbon dioxide (CO₂). These complexes can catalyze the degradation of harmful organic and inorganic pollutants in air and water by processes such as oxidation, reduction and photocatalysis. They are important in environmental remediation, turning toxic substances into less harmful products. Moreover, transition metal catalysts are intensively studied for CO₂ reduction to convert this greenhouse gas into valuable chemicals and fuels like carbon monoxide, methanol, and hydrocarbons. This helps not only in fighting climate change but also in designing sustainable chemical processes. Their high efficiency, selectivity and ability to work under mild conditions make transition metal complexes useful tools in the advancement of green chemistry and the development of environmentally friendly industrial practices.

4.4 Pharmaceutical Synthesis: Transition metal complexes have been very important in pharmaceutical synthesis as metal catalyzed cross-coupling reactions are available to construct complex drug molecules in an efficient manner. Reactions such as Suzuki, Heck, Sonogashira and Buchwald Hartwig coupling (Hartwig, 2008) can lead to the formation of carbon-carbon and carbon heteroatom bonds with impressive selectivity. Metals such as palladium, nickel and copper are commonly used because they provide good selectivity and functional group

tolerance. These catalytic processes enable multistep syntheses by allowing the target compounds to be obtained in fewer reaction steps.

Thus, they enhance the efficiency of the overall production, maximize the product output and minimize the production of undesired by-products. The employment of such catalysts also contributes to greener pharmaceutical production by lowering energy consumption and minimizing chemical waste. Therefore, metal-catalyzed cross-coupling reactions have revolutionized modern medicinal chemistry, and remain at the core of the development of safer and more sustainable strategies for drug synthesis.

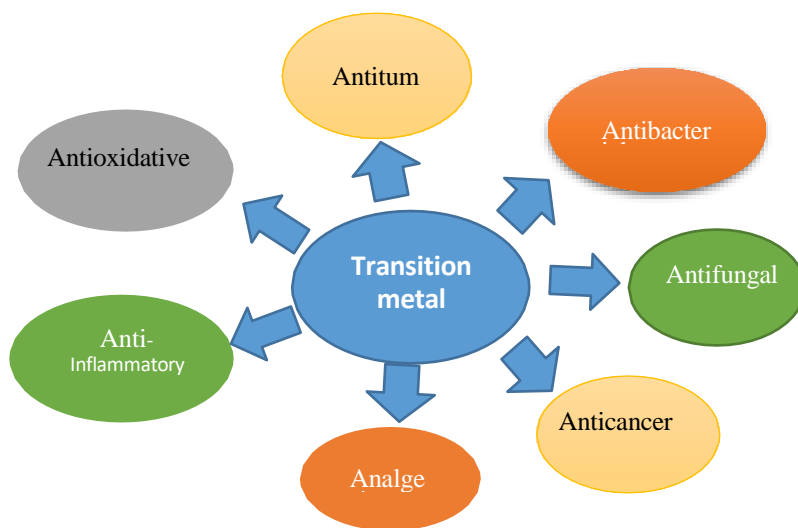


Fig. 4: Biological application of transition metal complexes.

5. Future Perspectives

In future research, there is a growing focus in transition metal chemistry on the development of efficient and sustainable catalytic systems. One of the major developments is the replacement of precious metals with earth-abundant metals such as iron, cobalt and nickel which are more economical and eco-friendly. In addition, machine learning and artificial intelligence are revolutionizing catalyst design with the ability to rapidly predict catalyst performance and optimize reaction conditions. Another promising direction is the development of bio-inspired and biomimetic systems that mimic natural enzyme processes and provide high selectivity under mild conditions. Further progress in ligand design and enhanced mechanistic understanding are predicted to improve catalytic performance and selectivity. The developments will not only enhance existing industrial processes but also open up new routes to sustainable chemical synthesis and thus drive innovation in pharmaceuticals, energy and environmental applications.

6. Conclusions

In conclusion, transition metal complexes still play an important role in the development of modern chemistry owing to their versatile and tunable properties. Their various applications in catalysis, industrial processes, environmental remediation and pharmaceutical synthesis render them important for basic and applied research. Their electronic and steric properties can be modified which enables a fine-tuning of their reactivity and selectivity. They are thus key tools in the field of chemical innovation. Further interdisciplinary work combining synthetic chemistry, detailed mechanistic studies and industrial engineering will be required to realize their full potential in the future. In addition to improving efficiency and sustainability, this collaborative approach will also encourage the development of new catalytic systems to meet future scientific and industrial challenges.

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