









Review Article 

Green Catalysis with Organometallic Complexes: Mechanistic Insights and Industrial Perspectives



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ABSTRACT

Green catalysis utilizing organometallic complexes represents a cornerstone of modern sustainable chemistry, offering significant advancements in environmentally friendly and resource-efficient chemical transformations. This review presents a comprehensive analysis of the mechanistic principles, catalytic performance, and industrial relevance of organometallic catalysts in green chemistry. Beginning with an overview of the role and importance of green catalysis, the discussion progresses to the classification, ligand design, and performance attributes, such as stability, selectivity, and tunability of organometallic complexes. Key mechanistic pathways, including oxidative addition, reductive elimination, insertion, and metal-ligand cooperation, are explored in detail, supported by insights from computational and spectroscopic studies. This review further highlights the application of these complexes in essential green transformations, including C-C coupling reactions, hydrogenation, hydrofunctionalization, and CO₂ utilization. Real-world industrial applications are examined through case studies in pharmaceuticals, polymer synthesis, and renewable feedstock conversion, illustrating both the potential and limitations of these catalysts at scale. Additionally, sustainability metrics such as the E-factor, turnover number, and green chemistry indicators are employed to assess the environmental and economic impacts. The review concludes with an exploration of ongoing challenges, such as catalyst deactivation, and discusses future directions involving renewable energy integration, catalyst design innovation, and the incorporation of artificial intelligence and machine learning for accelerated discovery. Collectively, this work underscores the pivotal role of organometallic catalysis in advancing green chemistry from mechanistic understanding to industrial implementation.

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1. Introduction

Green catalysis, a cornerstone of sustainable chemistry, encompasses the development and application of catalytic systems that minimize the environmental impact while maintaining or enhancing process efficiency. This concept emerged in response to the pressing need for environmentally benign chemical processes that align with the principles of green chemistry, such as reducing waste, improving atom economy, and avoiding the use of hazardous substances. Traditional catalytic methods, although effective, often rely on toxic solvents, harsh reaction conditions, and non-renewable raw materials, which contribute to ecological degradation and resource depletion [1]. Green catalysis seeks to address these challenges by employing eco-friendly solvents (*e.g.*, water, supercritical CO₂, or ionic

liquids), renewable feedstocks, and recyclable catalysts, including heterogeneous, bio-based, and organometallic systems. Green catalysis is crucial for several industrial applications, including precision chemical and pharmaceutical synthesis, polymer manufacturing, and environmental remediation [2]. It not only improves process sustainability, but also aids in energy conservation, cost reduction, and regulatory compliance. Moreover, recent advancements in mechanistic comprehension, nanocatalysis, and computational modeling have broadened the applicability and efficacy of green catalysts, facilitating their incorporation into contemporary production processes. Green catalysis embodies a revolutionary methodology that facilitates the shift towards a circular economy and a more sustainable and secure chemical sector [3]. Organometallic complexes are essential for promoting

sustainable chemistry because they provide efficient and selective catalytic routes for many chemical reactions. These complexes, distinguished by their metal-carbon bonds, function as essential catalysts in several green processes, including hydrogenation, hydroformylation, cross-coupling, and polymerization reactions. The distinctive reactivity and adjustable electronic and steric characteristics of organometallic compounds provide meticulous regulation of reaction processes, thereby augmenting product selectivity, minimizing by-products, and boosting atom economy, which are crucial criteria in green chemistry [4].

Moreover, several organometallic catalysts function in soft settings and require less energy input than conventional catalytic systems, thereby considerably diminishing the environmental impact of chemical production. The integration of earth-abundant and less toxic metals, such as iron, copper, and nickel, into organometallic frameworks has emerged as a sustainable alternative to conventional noble-metal catalysts, harmonizing with environmental and economic considerations. Organometallic complexes enhance the activation of inert bonds such as C-H and C-C, enabling more efficient synthesis techniques with reduced steps and minimized waste [4]. Recent advancements in ligand design, bolstered by computational chemistry and mechanistic investigations, have enhanced the versatility and stability of these complexes, facilitating their application in reusable and immobilized catalytic systems. Organometallic chemistry is a vital and advanced discipline that directly facilitates the creation of sustainable, innovative, and economically feasible chemical processes [5].

2. Organometallic Complexes as Catalysts

The scope of this review encompasses a comprehensive examination of organometallic

complexes as catalysts in the broader context of green and sustainable chemistry (Table 1). This study aims to elucidate the fundamental principles, mechanistic pathways, and practical applications of organometallic catalysis, highlighting its pivotal role in enabling environmentally benign and economically feasible chemical transformations. This review systematically explores various classes of organometallic catalysts, including those based on transition metals such as Pd, Ru, Ni, Fe, and Cu, with emphasis on their structural diversity, ligand design, and catalytic performance [4]. Special attention has been given to recent advancements in catalyst development that promote sustainability, such as the use of earth-abundant metals, recyclable catalytic systems, and solvent-free or aqueous reaction media. The objectives include critically analyzing the efficiency, selectivity, and stability of these catalysts in key green processes, such as cross-coupling, olefin metathesis, hydrogenation, and C-H activation reactions. Additionally, this review aims to identify emerging trends, current limitations, and future opportunities in the field, particularly in terms of scalability, reusability, and integration into industrial workflows [6]. By providing a detailed overview of both fundamental insights and applied aspects, this review intends to serve as a valuable resource for researchers and practitioners working at the interface between organometallic chemistry and sustainable chemical engineering, fostering innovation toward greener synthetic methodologies [7].

2.1. Classification and general features

Organometallic complexes, characterized by the existence of a metal-carbon bond with the carbon belonging to an organic moiety, can be categorized according to many criteria, including the nature of the metal center, type of coordinated ligands, and geometry or oxidation state of the metal.

Table 1. Comparative analysis of organometallic complexes as catalysts

Catalyst type	Metal center	Ligand system	Catalyzed reaction(s)	Catalytic efficiency (TON/TOF)	Reaction conditions	Industrial/Research applications	Advantages	Limitations	Ref.
Wilkinson's Catalyst	Rhodium (Rh)	Triphenylphosphine (PPh ₃)	Hydrogenation of alkenes	TON: ~10 ⁴	Mild temp and pressure	Fine chemical synthesis	High selectivity	Air-sensitive	[8]
Grubbs' Catalyst (1st Gen)	Ruthenium (Ru)	PCy ₃ , Cl, =CHPh	Olefin Metathesis	TOF: ~10 ⁵ h ⁻¹	Room temp and inert atm	Polymerization and pharma	Functional group tolerance	Limited thermal stability	[9]
Grubbs' Catalyst (2nd Gen)	Ruthenium (Ru)	NHC, Cl, =CHPh	Ring-Closing Metathesis	TOF: ~10 ⁶ h ⁻¹	20–60 °C	Drug synthesis, green chemistry	Improved activity & stability	Sensitive to water	[10]
Schrock Catalyst	Molybdenum (Mo)	Imido, alkoxide	Alkene Metathesis	TON: ~10 ³	Strict inert conditions	Specialty polymer production	High reactivity	Moisture-sensitive	[11]
Zeise's Salt	Platinum (Pt)	Ethylene, Cl ⁻	π-complexation & activation	Moderate	Ambient	Organometallic synthesis	Classic π-complex	Low catalytic versatility	[12]
Vaska's Complex	Iridium (Ir)	CO, PPh ₃ , Cl ⁻	Oxidative addition, CO binding	Low-moderate	Room temp, inert	Gas storage, teaching tool	Reversible binding	Poor industrial use	[13]
Monsanto Process Catalyst	Rhodium (Rh)	Iodide, CO	Carbonylation of methanol to acetic acid	TON: >10 ⁶	150–200 °C, 30–60 atm	Acetic acid production	High TON, selectivity	Corrosive environment	[14]
Wacker Catalyst	Palladium (Pd)	Cl ⁻ , Cu ²⁺ co-catalyst	Oxidation of ethylene to acetaldehyde	TOF: ~10 ³ –10 ⁴ h ⁻¹	Aqueous medium, O ₂	Large-scale acetaldehyde	Water-based system	Pd leaching	[15]
Crabtree's Catalyst	Iridium (Ir)	Cyclooctadiene, P(OEt) ₃	Hydrogenation (even hindered olefins)	TOF: ~10 ⁴	25–60 °C, H ₂ atm	Stereoselective hydrogenation	Tolerates functional groups	Air-sensitive	[16]
Ziegler-Natta Catalyst	Titanium (Ti), Al co-catalyst	Alkyl, chloride	Polymerization of olefins	TON: >10 ⁶	Ambient–high P & T	Polypropylene, polyethylene	Stereocontrol, high yield	Residual metal impurities	[17]

These complexes are primarily classified into main group organometallics, transition metal organometallics, and organometallics based on lanthanides or actinides [18]. Transition metal organometallic complexes are notably

important in catalysis because of their diverse oxidation states, coordination geometries, and ability to promote electron transfer processes. These complexes frequently incorporate ligands such as phosphines, carbonyls,

cyclopentadienyls, and alkyl or aryl groups, which may be customized to affect their electronic and steric characteristics, thereby altering the catalytic activity and selectivity [19]. Their tunability, achieved by metal selection and ligand design, permits precise control over reactivity, stability, and solubility. Furthermore, several organometallic compounds have distinct molecular architectures that facilitate mechanistic investigations and computational modeling to guide systematic catalyst design. Organometallic complexes are highly useful; certain types are susceptible to oxygen and moisture and require specific management. Nevertheless, continuous progress in ligand creation, environmentally-friendly solvent systems, and catalyst immobilization has consistently enhanced the durability and sustainability of organometallic catalysis, solidifying its pivotal position in both academic and industrial chemical synthesis [20].

2.2. Ligand design for green catalysis

Ligand design plays a critical role in advancing green catalysis by directly influencing the activity, selectivity, stability, and environmental compatibility of the organometallic catalysts. In the context of sustainable chemistry, ligands are not merely passive spectators, but also active participants that shape the electronic and steric environment of the metal center, thereby determining the efficiency and eco-friendliness of catalytic processes. A well-designed ligand can enable reactions to proceed under milder conditions, reduce the generation of hazardous by-products, and enhance the overall atom economy of the transformation [21]. Modern ligand design strategies focus on developing systems that are not only effective, but also derived from renewable resources, biodegradable, and non-toxic. For instance, bio-based ligands incorporating amino acids, carbohydrates, and other natural scaffolds have

garnered attention due to their inherent sustainability. Additionally, ligands that promote water solubility or function in biphasic systems allow for catalysis in aqueous media, further minimizing reliance on volatile organic solvents. Sterically demanding ligands, such as bulky phosphines or N-heterocyclic carbenes (NHCs), have been instrumental in enhancing catalyst lifetimes and suppressing undesired side reactions, thus improving the catalyst turnover numbers and recyclability [22].

Ligand design is crucial in green catalysis, as it stabilizes the metal centre and influences its electronic and steric surroundings, achieving high efficiency and selectivity. It determines factors such as redox potential, coordination geometry, and substrate reactivity, which directly impact catalytic turnover and sustainability. Modern methodologies focus on developing ligands that promote metal-ligand cooperation (MLC), allowing bond activation and supporting activities under moderate conditions [23].

Integrating donor-acceptor functions, such as N-heterocyclic carbenes, phosphines, and pincer ligands, facilitates precise electron density adjustment, reduces reaction conditions, and compatibility with environmentally friendly solvents. Bulky substituents provide steric control, enhancing stability and recyclability [24]. The creation of bio-inspired and sustainable ligands from renewable feedstocks signifies an effort to harmonize catalyst design with ecological principles. Ligand design is especially important for earth-abundant metals because it offsets their reduced inherent reactivity compared to noble metals [25].

Hemilabile ligands, which offer dynamic coordination properties, can facilitate key mechanistic steps, such as substrate binding and product release, while maintaining the overall complex integrity. Structural variety of ligands in organometallic catalysis are shown in **Figure 1**.

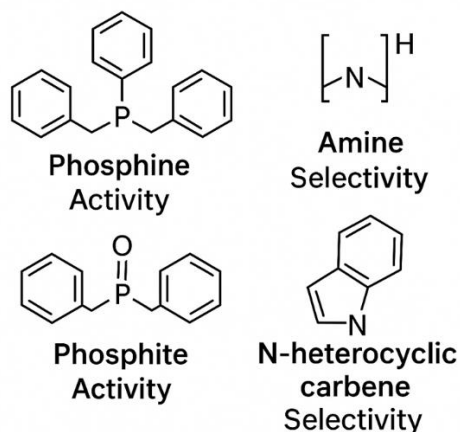


Figure 1. Structural variety of ligands in organometallic catalysis. Exemplary cases phosphine, amine, phosphite, and N-heterocyclic carbene demonstrate the impact of ligand design on catalytic activity and selectivity, emphasizing their function in optimizing reaction efficiency and results

Computational tools and mechanistic studies have become indispensable in the rational design of such ligands, allowing for the fine-tuning of ligand–metal interactions to achieve optimal catalytic outcomes. Overall, innovative ligand design is essential for the development of green catalytic systems, enabling the creation of more selective, efficient, and environmentally friendly chemical processes [26]. The structural and functional diversity of ligands used in organometallic catalysis shows how their electronic and steric properties influence activity, selectivity, atom economy, and recyclability. By incorporating abundant, biocompatible, or renewable scaffolds, ligand design plays a crucial role in advancing green catalysis and reducing the environmental impact, as shown in Figure 2.

3. Mechanistic Insights into Green Organometallic Catalysis

The principles of stability, selectivity, and tunability are fundamental for understanding

and optimizing the mechanisms underlying green organometallic catalysis. Mechanistic insights into these catalytic systems reveal that achieving high stability is crucial for catalyst longevity, recyclability, and economic feasibility, particularly in environmentally conscious processes. Stability is largely governed by the robustness of the metal–ligand framework and the resistance of the complex to decomposition under operational conditions, such as in the presence of air, moisture, or high temperatures [27]. Selectivity, another critical parameter, is intimately linked to the catalyst's ability to favor one reaction pathway over others, thereby minimizing side product formation and improving atom economy. In organometallic catalysis, selectivity often arises from the finely tuned steric and electronic properties of the ligand environment, which guide substrate orientation and transition state stabilization. The ability to systematically modify the catalytic behavior through structural alterations enables precise control over the reactivity, selectivity, and kinetic profiles.


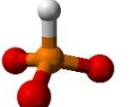
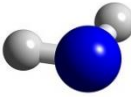

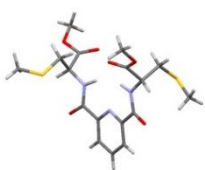
Ligands	Features	Impact on Green Catalysis
 Phosphine	Tunable steric/electronic properties	Enhance activity, control reaction rates
 Phosphite	Electron-withdrawing, Strong π -acceptors, flexible structures	Improve atom economy, reduce by-products
 Amine	Abundant, biocompatible, mild donors	Increase selectivity, eco-friendly sourcing
 N-Heterocyclic Carbene	Strong σ -donors, stable under conditions	High selectivity, recyclable catalysts
 Bio-inspired ligands	Derived from natural scaffolds	Renewable, biodegradable, sustainable use

Figure 2. Ligand design strategies for green catalysis. Representative classes of ligands phosphine, phosphite, amine, N-heterocyclic carbene, and bio-inspired ligands are compared based on their features and impact on catalytic sustainability

This is achieved by varying the metal centers, ligand types, coordination geometries, and oxidation states, which collectively influence key mechanistic steps, such as oxidative addition, migratory insertion, transmetalation, and reductive elimination [28]. Such mechanistic flexibility is essential for adapting catalysts to diverse substrates and reaction conditions, especially in solvent-free systems or aqueous or ionic liquid media preferred in green chemistry. Advanced spectroscopic techniques, kinetic modeling, and computational chemistry have significantly enhanced our ability to probe these mechanistic aspects, facilitating the rational design of more efficient, selective, and sustainable organometallic catalysts. Overall, a deep mechanistic understanding of the stability,

selectivity, and tunability forms the backbone of innovation in green organometallic catalysis, guiding the development of cleaner and more efficient chemical processes [29].

3.1. Oxidative addition and reductive elimination

Oxidative addition and reductive elimination are fundamental and often complementary mechanistic steps in organometallic catalysis, particularly processes relevant to green chemistry. These two elementary reactions involve changes in the oxidation state and coordination number of the metal center and are central to many catalytic cycles such as cross-coupling, hydrogenation, and C-H activation. In oxidative addition, a low-valent metal complex reacts with a substrate typically containing a polar or non-polar covalent bond,

such as H-H, C-X, or C-H, resulting in the insertion of the metal into that bond [30]. This step increases the oxidation state of the metal by two units and its coordination number, thereby forming a higher-valent metal complex with new metal-ligand bonds. This transformation is crucial for activating otherwise inert molecules under mild and sustainable conditions [31]. In contrast, reductive elimination involves a reverse process: two ligands bound to a metal center couple to form a new bond and are eliminated from the coordination sphere of the metal, thereby decreasing the oxidation state and coordination number of the metal [32]. Reductive elimination is often the key product-releasing step in many catalytic cycles and is heavily influenced by the electronic and steric environments created by the surrounding ligands [33]. The efficiency and selectivity of oxidative addition and reductive elimination can be tuned through ligand design, choice of metal, and reaction conditions. In green catalysis, promoting these transformations under mild, solvent-free, or aqueous conditions is of great importance, as it enhances atom economy and reduces the need for hazardous reagents or extreme conditions. A mechanistic understanding of these steps not only facilitates the design of more sustainable catalytic processes but also enables the development of new methodologies for forming carbon-carbon and carbon-heteroatom bonds with high efficiency and minimal environmental impact [34,35]. The oxidative addition step, a pivotal process in transition metal catalysis, involves the cleavage of a σ -bond and the formation of two new metal-ligand bonds. This step enhances the electron density at the metal center, thereby activating it toward subsequent transformations. The process is influenced by both steric and electronic factors, with electron-rich and coordinatively unsaturated metal complexes particularly adept at undergoing oxidative addition. Recent comparative studies focusing on catalytic performance metrics have substantiated the mechanistic importance of

oxidative additions. For example, nickel-palladium bimetallic nanoparticle catalysts (Ni-Pd/MWCNTs) in Sonogashira cross-coupling achieved a TON of $\sim 7,200$ and TOF of $\sim 21,600$ h^{-1} under ligand- and copper-free conditions [36]. Meanwhile, palladium catalysts featuring electronically flexible PYA ligands demonstrated turnover numbers of up to $\sim 7,300$ with TOFs approaching $\sim 9,000$ h^{-1} in C-C bond α -arylation [37]. Furthermore, state-of-the-art heterogeneous Pd(0) systems anchored on aza-ligand-functionalized supports have TONs as high as $\sim 89,000$ [38]. These data indicate that enhancements in the oxidative addition efficiency directly correlate with superior catalytic productivity across both homogeneous and heterogeneous catalyst platforms.

Figure 3 visually represents a redox reaction involving two species: A and B. In this process, species A undergoes oxidation, losing electrons (denoted as $-e^-$) and becoming positively charged (A^+), while species B undergoes reduction, gaining those electrons and becoming negatively charged (B^-). The diagram emphasizes the inverse relationship between oxidation and reduction: oxidation involves a loss of electrons and an increase in oxidation number, while reduction involves a gain of electrons and a decrease in oxidation number.

3.2. Insertion and elimination pathways

The insertion and elimination pathways are central mechanistic features in organometallic catalysis and play a vital role in controlling the outcome and efficiency of numerous green chemical transformations (**Table 2**). Insertion reactions typically involve the migration of a ligand, such as an alkyl or hydride group, from the metal center into a coordinated unsaturated molecule, such as an alkene, alkyne, carbon monoxide, or carbon dioxide. This process, often referred to as migratory insertion, results in the formation of a new covalent bond between the migrating group and the inserted molecule, while the metal center retains coordination with the newly formed ligand [39].

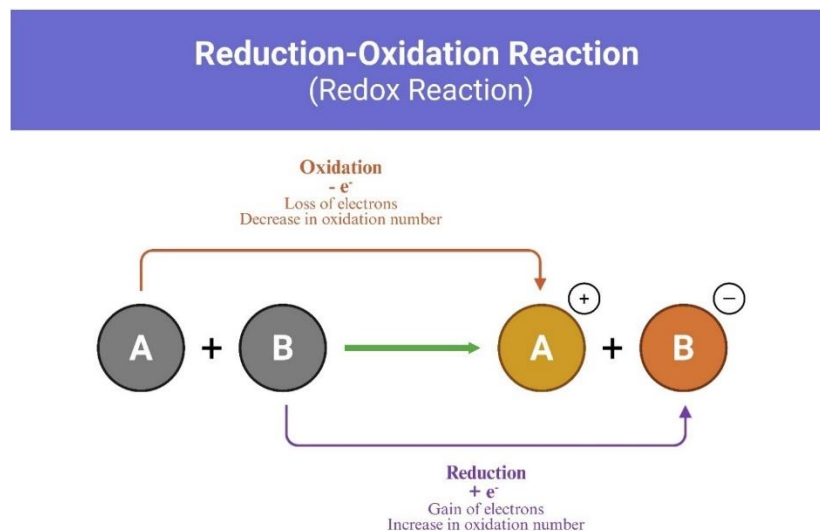


Figure 3. Illustration of a reduction-oxidation (Redox) reaction mechanism

These reactions are key to carbon–carbon and carbon–heteroatom bond formation in processes such as olefin polymerization, hydroformylation, and carbonylation. In contrast, elimination pathways involve the loss of small molecules from the metal coordination sphere, often resulting in the formation of a metal–ligand multiple bond or vacant coordination site that can facilitate subsequent catalytic steps. Among these, β -hydride elimination is particularly important, wherein the β -hydrogen from an alkyl ligand is transferred to the metal, forming a metal–hydride and an alkene [40]. This step is crucial in catalytic cycles, such as dehydrogenation, isomerization, and alkene metathesis. Both the insertion and elimination pathways are highly sensitive to the steric and electronic environments provided by the ligands and the nature of the metal center. In the context of green catalysis, optimizing these pathways allows for more selective and atom-economical reactions under mild and less energy-intensive conditions. The ability to control and predict these mechanistic events through ligand and metal design not only enhances catalytic

performance, but also supports the broader goals of sustainability, such as minimizing waste and avoiding toxic intermediates or by-products [41].

3.3. Role of metal–ligand cooperation

Metal–ligand cooperation (MLC) is an advanced concept in organometallic chemistry that has emerged as a powerful strategy for enhancing catalytic performance, particularly in the context of green and sustainable catalysis.

Unlike traditional views, where ligands serve merely as spectators or structural supports, MLC emphasizes the active, synergistic participation of ligands in the catalytic cycle alongside the metal center [52]. This cooperative interaction can occur in various forms, including reversible bond formation or cleavage, proton shuttling, redox non-innocence, and electronic delocalization, all of which facilitate challenging transformations under milder and more environmentally benign conditions. For instance, ligands capable of reversible aromatization–dearomatization or

Table 2. Insertion and elimination pathways in organometallic catalysis: mechanisms, green chemistry relevance, and industrial applications

Pathway	Organometallic Complex	Metal Center	Ligands	Reaction Type	Mechanism	Green Chemistry Advantage	Industrial Application	Limitations	Ref.
1,1-Insertion	Wilkinson's Catalyst	Rh(I)	PPh ₃ , Cl	Hydrogenation	Insertion of alkene into Rh-H bond	Atom economy, mild conditions	Fine chemical synthesis	Sensitive to air/moisture	[42]
1,2-Insertion	Schrock Alkylidene Complex	Mo(VI)	Imido, alkoxide	Olefin Metathesis	Formation of metallacyclobutane via 1,2-insertion	Solvent-free polymerization	Specialty polymers	Air-sensitive	[43]
Migratory Insertion (CO)	Vaska's Complex	Ir(I)	CO, PPh ₃ , Cl	Carbonylation	Alkyl group migrates to CO ligand	Minimizes waste, high selectivity	Carbonylation of alcohols	Limited scalability	[44]
β-Hydride Elimination	Pd(II)-Alkyl Complex	Pd(II)	PPh ₃ , Cl	Alkene formation	Elimination of β-H atom forms alkene	Step in catalytic cycles, no toxic reagents	Heck & Suzuki coupling	Competing side reactions	[45]
Reductive Elimination	Pd(II), Rh(III) Complexes	Pd(II), Rh(III)	Bidentate phosphines	C-C, C-X bond formation	Two ligands couple and are eliminated	Atom efficiency, minimal by-products	Cross-coupling, C-N formation	Requires ligand tuning	[46]
Oxidative Addition / Reductive Elimination Pair	Pd(PPh ₃) ₄	Pd(0)	Phosphines	C-X bond activation & coupling	Key cycle in cross-couplings	Solvent recovery, recyclable catalyst	Pharma & agrochemical industries	Ligand-sensitive pathway	[47]
α-Elimination	Ni(II)-Hydride Complex	Ni(II)	Diphosphines	Carbene formation	Loss of α-H to form carbene	Generates reactive intermediates	Synthesis of cyclopropanes	Competing β-H elimination	[48]

Insertion into M-H bond	Crabtree's Catalyst	Ir(I)	NHC, P(OEt) ₃	Hydrogenation	Alkene inserts into M-H bond	High stereoselectivity, fewer steps	Syntheses of alcohols	Cost and sensitivity	[49]
Elimination via β-heteroatom	Pd(II)-OR Complex	Pd(II)	Phosphine, alkoxide	Dehydration/Dehydrohalogenation	Elimination of -OH or -X from β-position	Avoids strong acids, eco-friendly	Green dehydration reactions	Moderate stability	[50]
σ-Bond Metathesis (Insertion-like)	Early transition metal complexes	Zr(IV), Ti(IV)	Alkyl, Cl, Cp	Alkane activation	Ligand exchange with C-H bond	No change in oxidation state	Polyolefin functionalization	Limited to certain metals	[51]

proton-responsive behavior can stabilize reactive intermediates, assist in substrate activation, and enable multistep reactions in a concerted manner, thereby enhancing both reactivity and selectivity. MLC is particularly advantageous for the activation of inert bonds, such as C-H, N-H, and O-H, which are otherwise difficult to functionalize without harsh reagents or conditions [53,54]. By enabling these processes at lower temperatures and with improved atom economy, MLC significantly contributes to reducing the energy input and environmental footprint of catalytic reactions. Moreover, the integration of redox-active or pH-switchable ligands into organometallic complexes opens new avenues for catalyst design with tunable activity and selectivity, adaptability to various green solvents, and renewable feedstocks. Mechanistic investigations, including spectroscopic, kinetic, and computational studies, have continued to unravel the complex interplay between metals and ligands, allowing for the rational design and optimization of MLC-based systems. Ultimately,

metal-ligand cooperation represents a paradigm shift in catalysis, offering transformative opportunities for the development of highly efficient, selective, and sustainable catalysts [55].

Figure 4 highlights the diverse functions of metal-ligand cooperation (MLC) within organometallic complexes, which are essential for catalytic activity and efficiency. The central molecular structure represents a metal-ligand complex surrounded by key functional contributions of MLC, facilitating bond activation, stabilizing reactive intermediates, promoting reversible bond formation, improving selectivity, and enabling redox-neutral pathways. Additional roles include enhancing catalyst reactivity, supporting bifunctional catalysis, controlling reaction kinetics, mimicking enzymatic functionality, and enabling the activation of small molecules [54,56]. These cooperative interactions are fundamental to advancing sustainable and selective catalytic transformations in green chemistry and industrial applications.

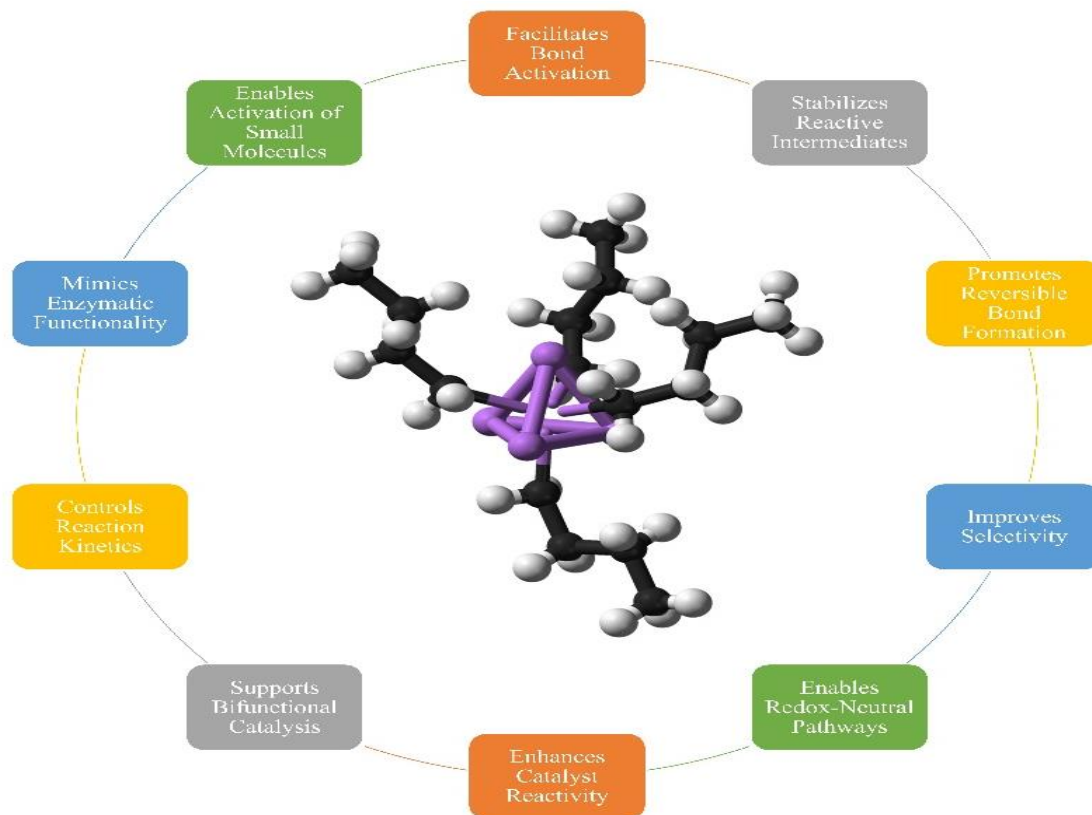


Figure 4. Multifaceted roles of metal-ligand cooperation in organometallic catalysis

3.4. Computational and spectroscopic studies

Computational and spectroscopic studies have emerged as complementary and indispensable tools in modern chemical and material research, providing deep insights into the structural, electronic, and dynamic properties of molecules and materials. Computational chemistry, encompassing methods such as density functional theory (DFT), molecular dynamics (MD), and quantum mechanical calculations, allows for the modeling and prediction of molecular behavior at the atomic level. These techniques are particularly valuable for elucidating reaction mechanisms, optimizing molecular geometries, and interpreting electronic structures, which are often inaccessible through experimental means alone [57]. Spectroscopic techniques, including nuclear magnetic resonance (NMR), infrared (IR), ultraviolet-visible (UV-Vis), and Raman spectroscopy, as well as more advanced methods such as X-ray photoelectron

spectroscopy (XPS) and electron paramagnetic resonance (EPR) offer empirical data that validate theoretical predictions. The integration of computational and spectroscopic approaches enables robust and multidimensional understanding of molecular systems. For instance, computational simulations can predict vibrational frequencies and electronic transitions, which can then be verified by IR and UV-Vis spectra, respectively. Similarly, NMR chemical shifts computed via quantum methods can be correlated with experimental spectra to confirm molecular conformations or tautomeric equilibria [58]. In catalysis and materials science, this synergistic approach has significantly advanced the characterization of active sites, design of functional materials, and interpretation of complex reaction pathways. Overall, the convergence of computational and spectroscopic studies fosters a more comprehensive and accurate portrayal of molecular phenomena, thereby accelerating the development of novel compounds and

technologies across various scientific disciplines [59].

4. Green Catalytic Transformations Using Organometallic Complexes

Organometallic complexes have become indispensable tools for enabling green catalytic transformations that align with the principles of sustainable chemistry, offering pathways for high-efficiency, low-waste, and energy-saving chemical processes. These transformations leverage the unique reactivity of metal-carbon bonds and the tunability of ligands to facilitate reactions with high atom economy, minimal by-product formation, and the use of environmentally benign solvents or solvent-free systems [60]. Notable green transformations catalyzed by organometallic complexes include cross-coupling reactions (*e.g.*, Suzuki, Heck, and Sonogashira couplings), which form C-C and C-heteroatom bonds under mild conditions, and have widespread applications in pharmaceuticals and fine chemicals. Similarly, olefin metathesis, often catalyzed by ruthenium or molybdenum complexes, is a highly atom-economic process that generates minimal waste and is used in the polymer synthesis and the valorization of bio-based feedstocks. Other essential green transformations include hydrogenation and hydroformylation reactions, in which transition metal complexes catalyze the addition of hydrogen or carbon monoxide to unsaturated substrates under milder conditions with improved selectivity [61].

The use of water-soluble catalysts, supported catalysts, and catalysts based on earth-abundant metals such as iron, cobalt, and nickel has further enhanced the environmental credentials of these transformations. Moreover, many organometallic-catalyzed reactions are now being conducted in green solvents, such as water, ethanol, or ionic liquids, and are designed for recyclability and reusability. Mechanistic insights and computational modeling continue to refine these systems, ensuring that they meet industrial requirements while adhering to green chemistry metrics. As a result, organometallic complexes play a central role in modern sustainable synthesis, driving

innovations that reduce ecological impacts while maintaining or improving chemical performance [62].

4.1. C-C coupling reactions

Carbon-carbon (C-C) coupling reactions represent the cornerstone of modern synthetic organic chemistry, enabling the efficient formation of complex molecular frameworks through the construction of new C-C bonds (Table 3). Suzuki-Miyaura, Heck, and Sonogashira reactions are among the most prominent and widely utilized C-C coupling reactions, all of which have revolutionized the synthesis of pharmaceuticals, natural products, agrochemicals, and advanced materials. These reactions typically employ transition metal catalysts, most notably palladium complexes, and proceed via well-defined mechanisms involving oxidative addition, transmetalation or carbometallation, and reductive elimination [63]. The Suzuki-Miyaura reaction couples aryl or vinyl boronic acids with aryl or vinyl halides under basic conditions, offering high functional group tolerance, mild reaction conditions, and scalability, making it ideal for constructing biaryl motifs and other conjugated systems [64]. The Heck reaction involves the coupling of alkenes with aryl halides to form substituted alkenes, often with excellent regio- and stereoselectivity, and is extensively used in the preparation of stilbenes, cinnamates, and other alkene derivatives [65].

Sonogashira coupling combines terminal alkynes with aryl or vinyl halides, typically in the presence of a palladium catalyst and copper co-catalyst, facilitating the synthesis of arylalkynes and enynes, which are valuable intermediates in organic electronics and medicinal chemistry [66].

The development of ligand design and catalyst modification strategies, including the advent of ligand-free, aqueous-phase, and recyclable catalytic systems, has significantly enhanced the efficiency, selectivity, and sustainability of these reactions. Moreover, recent advances in C-C coupling methodologies, including mechanochemical, electrochemical, and photoredox-assisted variants, continue to

Table 3. Overview of key C–C coupling reactions in organometallic catalysis

Coupling Reaction	Reactants	Catalyst (Metal)	base / Additive	Mechanism type	Green chemistry advantage	Application area	Ref.
Suzuki–Miyaura	Aryl/alkenyl halide + boronic acid	Pd, Ni	Base (K ₂ CO ₃ , NaOH)	Oxidative addition, transmetalation, reductive elimination	Water-compatible, mild conditions	API synthesis, agrochemicals	[69]
Heck Reaction	Aryl halide + alkene	Pd, Ni	Base (Et ₃ N, NaOAc)	Oxidative addition, migratory insertion, β-H elimination	No prefunctionalization of alkene	Steroidal & pharmaceutical intermediates	[70]
Sonogashira	Aryl halide + terminal alkyne	Pd–Cu co-catalyst	Amine (Et ₃ N)	Oxidative addition, transmetalation, reductive elimination	Room temp, fewer steps	Synthesis of alkynes in natural products	[71]
Stille Reaction	Aryl halide + organostannane	Pd	Base (often omitted)	Similar to Suzuki	Functional group tolerance	Natural products, OLED precursors	[72]
Negishi Reaction	Aryl halide + organozinc	Pd, Ni	May not require base	High reactivity, wide scope	Air-sensitive reagents	Total synthesis, material science	[73]
Kumada Reaction	Aryl halide + Grignard (R–MgX)	Ni, Pd	No base needed	Oxidative addition, transmetalation	High TON, fast kinetics	Polymers, agrochemicals	[74]
Ullmann Coupling	Aryl halide + aryl halide	Cu	Heat	Radical or oxidative pathway	Metal economy (Cu over Pd)	Dye and pigment manufacturing	[75]
Glaser Coupling	Terminal alkynes	Cu	O ₂ (oxidant)	Oxidative coupling	Oxidant = air, no extra reagents	DIY electronics, bioconjugation	[76]
C–H Activation Coupling	Aryl C–H + aryl halide	Pd, Rh, Ru	Directing group required	C–H activation, coupling	Step economy, less waste	Late-stage drug functionalization	[77]

expand the scope and applicability of these transformations [67]. Collectively, Suzuki, Heck, and Sonogashira couplings exemplify the power of transition metal-catalyzed strategies in forging C–C bonds with precision and have become indispensable tools in the arsenal of synthetic chemists [68].

4.2. Hydrogenation and transfer hydrogenation

Hydrogenation and transfer hydrogenation are fundamental and widely employed reactions in both academic and industrial chemistry for the reduction of unsaturated organic compounds

such as alkenes, alkynes, ketones, and imines to their corresponding saturated analogs. Hydrogenation, in its classical form, involves the addition of molecular hydrogen (H₂) across multiple bonds in the presence of a metal catalyst typically composed of transition metals such as Pd, Pt, Rh, or Ni [78].

These catalysts facilitate the heterolytic cleavage of H₂ and the subsequent transfer of hydrogen atoms to the substrate, resulting in high atom economy and excellent selectivity. Hydrogenation is critical for the large-scale synthesis of fine chemicals, petrochemicals, and active pharmaceutical ingredients, owing to its

simplicity, scalability, and efficiency. However, reliance on high-pressure hydrogen gas and precious metal catalysts can pose challenges related to safety, cost, and sustainability [79]. In contrast, transfer hydrogenation offers a milder and often safer alternative by employing hydrogen donors, such as isopropanol, formic acid, or sodium borohydride, instead of molecular hydrogen. This reaction typically proceeds via a catalytic cycle facilitated by metal complexes (commonly based on ruthenium, iridium, or iron) or organocatalysts, which mediate hydride and proton transfer processes. Transfer hydrogenation is particularly advantageous in asymmetric synthesis, in which chiral ligands can be employed to induce enantioselectivity in the reduction of prochiral substrates, leading to optically active alcohols and amines with high stereocontrol. Recent developments in catalyst design, including the use of earth-abundant metals, N-heterocyclic carbenes (NHCs), and metal–ligand cooperative systems, have significantly improved the activity, selectivity, and environmental compatibility of both hydrogenation and transfer hydrogenation reactions. These methodologies play a pivotal role in green chemistry, contributing to more sustainable and efficient synthetic processes in both laboratory and industrial settings [80].

4.3. Hydrofunctionalization

Hydrofunctionalization reactions, including hydroamination, hydroboration, hydrosilylation, and hydroalkoxylation, represent a powerful class of atom-economical transformations involving the addition of a hydrogen atom and functional group across unsaturated carbon–carbon bonds, such as alkenes or alkynes (Table 4). These reactions are instrumental in the direct formation of C–N, C–B, C–Si, and C–O bonds, offering efficient routes to structurally complex molecules with high regio- and stereoselectivity [81]. Hydroamination, for instance, enables the direct formation of amines from alkenes or alkynes

and amine nucleophiles, often catalyzed by early transition metals such as titanium, zirconium, or lanthanides, or more recently, by earth-abundant metals such as iron and manganese [82]. Hydroboration, pioneered by Brown, involves the syn-selective addition of boron and hydrogen across unsaturated bonds and serves as a key step in the synthesis of alcohols, amines, and other functionalized derivatives via subsequent oxidation or substitution reactions. The advancement of transition-metal catalysis, particularly involving rhodium, iridium, and copper complexes, has significantly broadened the scope and selectivity of these transformations [83].

Figure 5 outlines the hydrofunctionalization processes in organometallic catalysis, involving hydrogen-containing substances across unsaturated bonds. The left-hand side includes hydroamination, hydrosilylation, hydroboration, hydroformylation, and hydrocyanation, adding different functional groups such as amines, silanes, boranes, formyl, or nitriles. The right side includes hydroalkoxylation, hydrophosphination, hydrochlorination, hydrogenation, hydroselenation/thiolation, and the addition of ethers, phosphines, halides, hydrogen, or chalcogen species. These changes are crucial in green chemistry and industrial synthesis to produce compounds with high atom economy and selectivity. Mechanistically, hydrofunctionalization often proceeds via metal-hydride intermediates, π -complexation of the unsaturated substrate, and migratory insertion steps, with ligand design playing a crucial role in controlling reactivity and selectivity. Importantly, these reactions align well with the principles of green chemistry due to their high atom economy, minimal byproduct formation, and compatibility with sustainable catalytic systems. Consequently, hydrofunctionalization reactions are increasingly being applied in the synthesis of fine chemicals, pharmaceuticals, and polymers, making them indispensable tools in modern synthetic chemistry [84].

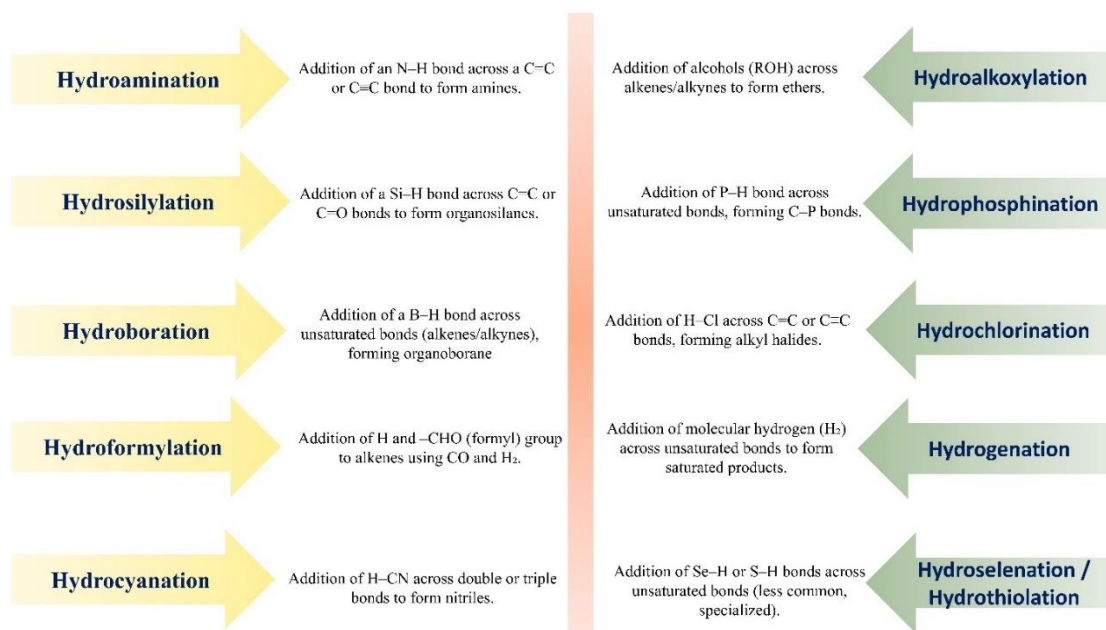


Figure 5. Overview of hydrofunctionalization reactions in organometallic catalysis

4.4. CO₂ activation and utilization

CO₂ activation and utilization have emerged as critical areas of research in contemporary chemistry, driven by the dual imperatives of mitigating climate change and developing sustainable sources of carbon for chemical synthesis. Despite its abundance and non-toxicity, carbon dioxide is a thermodynamically stable and kinetically inert molecule, necessitating the use of organometallic or enzymatic catalysts to enable its transformation into value-added products [94]. Transition metal complexes, particularly those containing metals such as nickel, cobalt, ruthenium, and copper, have demonstrated efficacy in

activating CO₂ through coordination to metal centers, thereby lowering the activation energy for the subsequent bond-forming steps. These systems have facilitated a range of transformations, including the carboxylation of organometallic reagents, reduction to formic acid, methanol, or methane, and cycloaddition reactions with epoxides to form cyclic carbonates. More recently, cooperative catalysis involving metal-ligand frameworks and frustrated Lewis pairs (FLPs) has expanded the scope of CO₂ functionalization under milder conditions [19]. Electrochemical and photochemical strategies employ renewable electricity or sunlight to drive the reduction of CO₂, offering an attractive route for carbon

Table 4. Hydrofunctionalization reactions catalyzed by organometallic complexes: mechanisms, green chemistry benefits, and industrial applications

Hydro functionalization Type	Reaction Description	Representative Metal Catalyst	Mechanistic Pathway	Green Chemistry Advantage	Industrial & Research Applications	Ref.
Hydroamination	Addition of N-H across C=C or C≡C bonds	Lanthanide (Yb, La), Ru, and Pd	Insertion into M-N bond followed by C-N bond formation	Atom economy, no by-products	Synthesis of amines, drug intermediates	[85]

Hydrosilylation	Addition of Si-H to alkenes/alkynes or carbonyls	Pt (Karstedt's), Rh, and Fe	Migratory insertion followed by reductive elimination	Solvent-free & selective	Silicon-based materials, fine chemicals	[86]
Hydroboration	Addition of B-H to unsaturated bonds	Rh, Ir, and Cu	Syn-addition via π -complex and M-B bond formation	High regioselectivity, mild conditions	Precursors to organoboron compounds	[87]
Hydroformylation	Addition of H and -CHO across alkenes (oxo process)	Rh-phosphine complexes	Insertion of CO and alkene, followed by H addition	High atom economy, recyclable catalysts	Production of aldehydes, plasticizers	[88]
Hydrocyanation	Addition of H and -CN to alkenes	Ni(0), Pd(0)	Oxidative addition \rightarrow insertion \rightarrow reductive elimination	Avoids stoichiometric cyanide salts	Nitrile synthesis in agrochemicals	[89]
Hydroalkoxylation	Addition of alcohols across unsaturated bonds	Au, Pd, and Ru	Electrophilic activation or metal-alkoxide formation	No external base, fewer steps	Ether synthesis, fragrance industry	[90]
Hydrophosphination	Addition of P-H to C=C/C \equiv C bonds	Ti, Zr, and Ni	Nucleophilic or insertion-based mechanism	No oxidants, good P-C bond selectivity	Ligand precursors, flame retardants	[91]
Hydrochlorination	Addition of H-Cl to alkenes/alkynes	Pd, Au, and Fe	Electrophilic activation and Cl transfer	Solvent-less pathways possible	PVC precursor production	[92]
Hydrogenation	Addition of H ₂ to alkenes/alkynes/carbonyls	Rh, Ru, Ir, and Fe	Metal-hydride formation & alkene insertion	No solvent, high selectivity	Pharmaceutical intermediates, margarine	[93]

recycling. Despite considerable progress, challenges remain in achieving high selectivity, catalytic turnover, and energy efficiency, especially on an industrial scale. Nonetheless, the development of efficient CO₂ activation and utilization strategies represents a promising avenue toward closing the carbon cycle and achieving a circular economy, contributing to both environmental sustainability and the advancement of green synthetic methodologies [95].

5. Industrial Applications and Case Studies

The fields of green catalysis and organometallic chemistry underscore the transition from laboratory-scale innovations to commercially viable and environmentally sustainable processes (Table 5). The integration of catalytic technologies into industrial settings has led to significant improvements in efficiency, selectivity, and waste reduction across diverse sectors such as pharmaceuticals, petrochemicals, agrochemicals, and polymer manufacturing [96]. Notable case studies include the Monsanto and Cativa processes for acetic acid production, which utilize rhodium and iridium catalysts, respectively, to achieve high turnover numbers and minimal by-product formation under relatively mild conditions [97].

Similarly, the hydroformylation of alkenes catalyzed by cobalt or rhodium complexes has been widely implemented for the synthesis of aldehydes and alcohols, which are key intermediates in the production of plasticizers, detergents, and solvents. In the pharmaceutical industry [98], asymmetric hydrogenation catalyzed by chiral rhodium or ruthenium complexes has enabled the enantioselective synthesis of active pharmaceutical ingredients (APIs), as exemplified by the industrial-scale production of (S)-metolachlor and L-DOPA [99]. Furthermore, olefin metathesis, facilitated by ruthenium-based Grubbs catalysts, has been successfully scaled up for the manufacture of specialty chemicals and advanced materials. Case studies also highlight the adoption of transfer hydrogenation and CO₂ utilization in continuous-flow systems, enhancing process safety and scalability [100]. These industrial implementations not only demonstrate the practical utility of organometallic catalysts, but also reflect a broader commitment to green chemistry principles, including atom economy, energy efficiency, and the use of non-toxic reagents and renewable feedstocks. Collectively, these examples reinforce the role of catalysis as a cornerstone of sustainable industrial chemistry, bridging the gap between academic discovery and commercial application [101].

Table 5. Comparative assessment of traditional catalytic systems versus organometallic complexes in green catalysis

Parameter	Traditional catalysis	Organometallic complexes in green catalysis
Catalyst source	Often mineral acids, toxic metals	Transition metals with eco-friendly ligands
Reaction medium	Organic solvents (volatile and toxic)	Water, supercritical CO ₂ , and ionic liquids
Selectivity	Moderate, leads to by-products	High chemo-, regio-, and stereoselectivity
Energy requirement	High temperature and pressure	Mild conditions (lower T & P)
Environmental impact	Generates hazardous waste	Reduced waste and recyclable catalysts
Sustainability	Limited	Enhanced by renewable feedstocks and atom economy

5.1. Pharmaceutical and fine chemicals production

Pharmaceutical and fine chemical production rely heavily on organometallic catalysis and green synthetic methodologies to achieve efficient, selective, and sustainable transformations. The synthesis of active pharmaceutical ingredients (APIs) and high-value intermediates requires stringent control over chemo-, regio-, and stereoselectivity, which is effectively enabled by well-designed catalytic systems, particularly those based on transition metals such as palladium, rhodium, ruthenium, and iridium [102]. Cross-coupling reactions such as Suzuki–Miyaura, Heck, and Buchwald–Hartwig amination are extensively employed to construct complex carbon–carbon and carbon–heteroatom bonds in a modular and high-yielding manner, streamlining synthetic routes while minimizing waste [103]. Asymmetric catalysis, including enantioselective hydrogenation and hydroamination, is pivotal for generating chiral centers in drug molecules with high enantiomeric excess, often under mild reaction conditions that are compatible with sensitive functional groups [104].

Furthermore, flow chemistry and microwave-assisted catalysis are increasingly being integrated into pharmaceutical synthesis, offering improved reaction rates, scalability, and safety. In the realm of fine chemicals, including agrochemicals, flavors, fragrances, and dyes, similar catalytic principles are applied to tailor molecular architectures with precision and economy. The adoption of green solvents, recyclable catalysts, and bio-based feedstocks further aligns these synthetic processes with the principles of green chemistry [105]. Additionally, recent developments in biocompatible and water-tolerant catalytic systems have expanded the applicability of organometallic methods for late-stage functionalization of complex biomolecules. Overall, catalysis in pharmaceutical and fine chemical production exemplifies the confluence of innovation, sustainability, and efficiency, reflecting a paradigm shift toward cleaner and

more responsible chemical manufacturing [106].

5.2. Polymerization processes

Polymerization processes involve a diverse array of chemical reactions that convert monomeric units into macromolecular polymers with specific architectures, properties, and functionalities. These processes are broadly categorized into addition (chain-growth) and condensation step-growth polymerizations, each governed by distinct mechanistic pathways and kinetic profiles [107]. In chain-growth polymerization, exemplified by free-radical, cationic, anionic, and coordination polymerizations, such as Ziegler–Natta and metallocene catalysis, polymer chains grow rapidly through the successive addition of monomers to an active center [108]. This method is widely used for the synthesis of commodity polymers such as polyethylene, polypropylene, and polystyrene. In contrast, step-growth polymerization involves the gradual formation of bonds between bifunctional or multifunctional monomers to produce materials such as polyesters, polyamides, and polyurethanes. Modern advancements in polymer chemistry have introduced controlled/"living" polymerization techniques such as atom transfer radical polymerization (ATRP), reversible addition fragmentation chain-transfer (RAFT) polymerization, and ring-opening polymerization (ROP) which allow for precise control over molecular weight, polydispersity, and block copolymer architecture [109]. Moreover, sustainable polymerization strategies, including the use of bio-based monomers and green solvents, are gaining traction in response to environmental concerns and the need for circular polymers. The integration of catalysis, computational modeling, and real-time spectroscopic monitoring continues to revolutionize polymerization processes, enabling the design of next-generation polymers tailored for high-performance applications in the biomedicine,

electronics, packaging, and aerospace industries [110].

Polymerization processes entail covalent bonding of small monomers, resulting in the formation of macromolecules or polymers that exhibit distinct structural and functional characteristics. These processes are categorized into chain-growth polymerization and step-growth polymerization [111].

Chain-growth polymerization is characterized by the swift elongation of polymer chains via the incorporation of activated monomer units, facilitating the achievement of high molecular weights even at low conversion rates. Step-growth polymerization is characterized by the incremental reaction of bifunctional or multifunctional monomers, necessitating a high conversion rate to obtain high-molecular-weight polymers [112]. Catalysts, especially organometallic complexes, are essential in contemporary polymerization processes, facilitating precise control over stereochemistry, molecular weight distribution,

and polymer architecture. Recent advances have highlighted the importance of green polymerization strategies, which include solvent-free systems, aqueous-phase reactions, renewable monomers, and recyclable catalysts. Controlled polymerization methods such as ATRP, RAFT, and ROP enable the precise tailoring of polymer microstructures, facilitating advancements in sustainable materials and biomedical applications.

Figure 6 shows the hydrogel synthesis process using photo-initiated free radical polymerization. The process involved mixing monomers NIPAM, HEMA, and NVP with a photoinitiator in deionized water, sonicating for uniform dispersion, nitrogen purging to eliminate oxygen, and exposure to UV light for 30 min. The resulting hydrogel was then purified by dialysis in DI water for 3 days and freeze-dried for 3 days to obtain a dry hydrogel product. This process creates a biocompatible and stable polymer network suitable for biomedical applications [113].

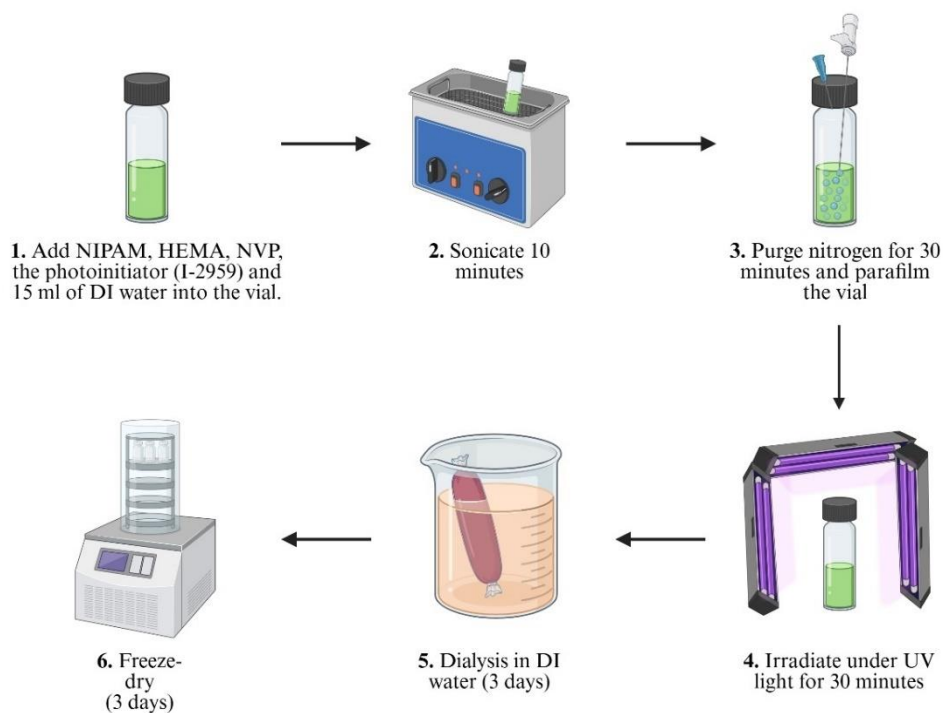


Figure 6. Stepwise schematic of the polymerization process using photo-initiated polymerization

5.3. Bio-based feedstocks and renewable substrates

The utilization of bio-based feedstocks and renewable substrates represents a pivotal shift toward sustainable chemical synthesis, addressing the environmental and economic limitations associated with fossil-derived resources. These feedstocks, derived from biomass such as lignocellulosic materials, starch, sugars, plant oils, and algae, offer renewable and often biodegradable alternatives for the production of fuels, chemicals, and polymers [114]. Lignocellulosic biomass composed of cellulose, hemicellulose, and lignin is particularly attractive because of its abundance, low cost, and minimal competition with food sources. Through processes such as enzymatic hydrolysis, pyrolysis, and fermentation, these raw materials can be transformed into platform chemicals like bioethanol, lactic acid, succinic acid, and 5-hydroxymethylfurfural (HMF), which serve as precursors for a wide range of value-added products [115]. Recent advances in metabolic engineering, synthetic biology, and biocatalysis have significantly improved the efficiency of microbial and enzymatic systems in converting biomass into industrially relevant compounds. Additionally, the integration of green chemistry principles, such as solvent-free reactions and energy-efficient processes, further enhances the environmental performance of bio-based production routes. Despite the challenges related to feedstock variability, supply chain logistics, and processing costs, the growing demand for carbon-neutral and circular economy solutions is driving innovation and investment in this sector. As policies and regulations increasingly favor sustainable materials, bio-based feedstocks are poised to play a central role in the transition to a greener and more resilient chemical industry [116].

5.4. Industrial challenges and success stories

The industrial implementation of green catalysis and sustainable chemical processes faces several formidable challenges; however, it

is also marked by notable success stories that exemplify the feasibility and benefits of environmentally benign practices. One of the primary challenges is the scalability and economic viability of green catalytic systems, which often require expensive or rare metal catalysts, specialized reaction conditions, or intensive purification protocols [117]. Additionally, the heterogeneity of bio-based feedstocks, regulatory hurdles, and inertia of existing petrochemical infrastructure hinder rapid industrial transition. Despite these obstacles, numerous success stories underscore the transformative potential of green catalysis. For instance, metathesis reactions catalyzed by ruthenium-based Grubbs catalysts have been successfully commercialized for the synthesis of specialty chemicals and pharmaceuticals, offering high atom economy and reduced waste. Similarly, BASF and other chemical giants have adopted enzymatic and biocatalytic routes for the production of fine chemicals such as acrylamide and chiral intermediates, showcasing the economic and environmental benefits of biotransformations [118]. The implementation of CO₂ utilization technologies, such as Covestro's use of CO₂ as a feedstock for polycarbonate polyols, demonstrates the industrial potential for greenhouse gas valorization. Moreover, the integration of green solvents such as supercritical CO₂, ionic liquids, and deep eutectic solvents into manufacturing processes highlights the industry's shift toward safer and more sustainable reaction media. These success stories not only validate the practical applicability of green technologies, but also inspire continued innovation in overcoming existing barriers, ultimately paving the way for a more sustainable and circular chemical industry [119].

6. Sustainability Assessment and Metrics

Sustainability assessment and metrics play a pivotal role in evaluating the environmental, social, and economic impacts of human activities, technologies, and policies to promote responsible development and resource use. These assessments provide a structured

framework for measuring and comparing sustainability performance across various sectors, including industry, agriculture, urban planning, and energy systems [120]. Sustainability metrics encompass quantitative and qualitative indicators that reflect key dimensions such as greenhouse gas emissions, water and energy consumption, biodiversity conservation, social equity, and economic viability. Life Cycle Assessment (LCA), Ecological Footprint Analysis, and the Triple Bottom Line (TBL) approach are widely recognized tools used to assess the sustainability of products, processes, and services throughout their life cycles [121]. The integration of these metrics into decision-making processes enables policymakers, businesses, and stakeholders to identify trade-offs, set benchmarks, and track progress toward sustainability goals such as those outlined in the United Nations Sustainable Development Goals (SDGs). Furthermore, the advancement of data analytics, modeling techniques, and sustainability reporting standards has significantly enhanced the ability to monitor complex systems and make informed, transparent decisions. Ultimately, sustainability assessments and metrics serve not only as diagnostic tools but also as guiding instruments for fostering innovation, minimizing adverse impacts, and ensuring long-term ecological and societal well-being [122].

Complexes are measured using key metrics, such as atom economy (how efficiently reactants are used), E-factor (amount of waste per product), and process mass intensity or PMI (total materials used per product) [123]. In the pharmaceutical sector, the E-factor typically ranges from 25 to 100 kg of waste per 1 kilogram of medicine, with current research indicating that approximately 120 kg of materials, predominantly solvents, are utilized to produce just 1 kg of a product. Palladium (Pd) and iridium (Ir), as precious metal catalysts, entail significant environmental costs, necessitating up to 72,700 and 216,000 MJ of energy per kilogram for production, respectively, predominantly from mining and processing activities [124,125]. Improvements

in recycling, renewable energy use, and a shift toward cheaper, earth-abundant metals are helping to reduce these impacts. These sustainability metrics not only highlight the challenges, but also guide the development of greener, more efficient organometallic catalysts for the industry [126].

7. E-factor, Turnover Number, Turnover Frequency

E-factor, Turnover Number (TON), and Turnover Frequency (TOF) are critical metrics in green chemistry and catalysis, serving as quantitative tools to evaluate the efficiency, sustainability, and environmental impact of chemical processes [127]. The E-factor environmental factor (E-factor), defined as the mass ratio of the waste generated to the desired product, provides a direct measure of the environmental footprint of a chemical reaction. Lower E-factors indicate more sustainable processes with minimal waste generation, which is especially important in the pharmaceutical and fine chemical industries, where waste disposal is costly and environmentally challenging [128]. The TON refers to the number of moles of substrate that a single mole of the catalyst can be converted into a product before becoming inactive. It measures the catalytic efficiency over the entire lifespan of the catalyst and is especially significant for determining the long-term viability of a catalyst in industrial applications [127]. TOF, which is closely related to the TON, quantifies the number of catalytic cycles that occur per unit time, typically expressed as moles of product formed per mole of catalyst per unit time (*e.g.*, per second or per hour). TOF is a kinetic parameter that reflects the speed at which a catalyst operates under given conditions. Together, these metrics allow chemists and chemical engineers to assess the environmental sustainability and operational performance of the catalytic processes. Integrating the E-factor, TON, and TOF into the process design enables the identification of inefficiencies, facilitates comparisons between alternative synthetic routes or catalysts, and guides the development

of greener, more cost-effective technologies. As the chemical industry increasingly aligns with the principles of green chemistry, these parameters are indispensable for achieving eco-efficient and economically viable transformations [129].

7.1. Green chemistry metrics in industrial catalysis

Green chemistry metrics in industrial catalysis are essential tools for evaluating and optimizing chemical processes in accordance with the principles of sustainability, efficiency, and environmental stewardship. In industrial settings, catalysis plays a pivotal role in reducing energy consumption, minimizing waste, and improving product selectivity, making the application of quantitative green chemistry metrics indispensable [130]. Key indicators, such as atom economy, E-factor (environmental factor), process mass intensity (PMI), turnover number (TON), and turnover frequency (TOF), provide comprehensive insights into the performance and ecological impact of catalytic reactions. For instance, atom economy assesses how efficiently raw materials are incorporated into the final product, promoting synthetic routes that reduce byproduct formation. The E-factor quantifies the ratio of waste to the desired product, highlighting the environmental burden associated with a given process, while PMI accounts for all input materials, offering a broader perspective on resource utilization [131]. TON and TOF provide critical data on catalyst efficiency and reaction kinetics, respectively, enabling process engineers to determine the catalyst's longevity and reaction throughput. The integration of these metrics facilitates the design and implementation of greener catalytic processes that not only comply with regulatory and safety standards, but also enhance economic competitiveness by reducing material costs and waste management expenses. Moreover, with the advent of computational modeling and real-time monitoring technologies, these metrics can now be applied dynamically throughout the

production lifecycle, enabling continuous improvement and innovation. Ultimately, green chemistry metrics in industrial catalysis are not merely evaluative tools but also strategic instruments that guide the transformation of traditional chemical manufacturing into more sustainable and responsible practices [132].

7.2. Environmental and economic impact

The environmental and economic impacts of chemical processes, technologies, and industrial practices have become focal points of contemporary scientific and policy discourse, particularly in the context of sustainable development. From an environmental perspective, chemical industries contribute significantly to issues such as greenhouse gas emissions, water and air pollution, hazardous waste generation, and depletion of non-renewable resources [133]. These impacts not only threaten ecological integrity, but also pose long-term risks to human health and biodiversity. Quantifying and mitigating these environmental burdens requires the integration of life cycle assessment (LCA), green chemistry metrics, and regulatory frameworks that promote cleaner production and resource efficiency. Economically, the drive toward sustainability can initially present cost challenges, including investments in cleaner technologies, renewable feedstocks, and waste management systems. However, in the long term, sustainable practices often lead to enhanced economic resilience through improved process efficiency, reduced raw material costs, lower environmental compliance expenses, and increased market competitiveness [134]. Moreover, companies that adopt environmentally responsible strategies are better positioned to meet rising consumer demand for green products and comply with evolving global environmental regulations. Therefore, the intersection of environmental and economic considerations is critical in shaping industrial innovation, policymaking, and corporate sustainability strategies. Ultimately, addressing environmental and economic impacts in tandem

ensures not only the viability of industrial operations, but also contributes to broader goals of ecological preservation, social responsibility, and intergenerational equity [135].

8. Challenges and Future Directions

Green catalysis using organometallic complexes represents a promising frontier in sustainable chemistry; however, it faces several significant challenges that must be addressed to fully realize its industrial potential. One of the primary obstacles is the limited stability and recyclability of many organometallic catalysts under operating conditions, which can lead to catalyst deactivation and increased process costs. Additionally, the use of precious or toxic metals such as palladium, platinum, or rhodium in many organometallic complexes raises environmental and economic concerns, particularly regarding metal recovery and lifecycle sustainability. Mechanistic insights into catalytic pathways remain critical for improving catalyst design; however, the complexity of reaction mechanisms, including issues of ligand dynamics, oxidative addition, and reductive elimination, often complicates mechanistic elucidation. Advanced spectroscopic techniques and computational modeling are increasingly employed to unravel these mechanisms, enabling the rational development of more robust and selective catalysts. From an industrial perspective, scalability, compatibility with green solvents or solvent-free systems, and integration with continuous-flow processes are essential for translating laboratory-scale success into commercial viability. Future directions in green catalysis with organometallic complexes will likely focus on the development of earth-abundant metal catalysts, ligand systems that enhance the selectivity and turnover numbers, and hybrid catalytic platforms that combine homogeneous and heterogeneous characteristics. Furthermore, the implementation of circular economy principles, such as catalyst recovery and reuse, is central to advancing industrial sustainability. Ultimately, the synergy between

mechanistic understanding and process engineering will shape the next generation of green catalytic technologies, bridging the gap between academic innovation and industrial application.

9. Conclusion

In conclusion, green catalysis with organometallic complexes represents a revolutionary method for attaining more sustainable and efficient chemical processes, merging the tenets of green chemistry with sophisticated catalytic design. The distinctive reactivity and adaptability of organometallic complexes offer considerable benefits for selectivity, reaction velocity, and functional group tolerance, which are crucial for waste reduction and energy conservation in industrial applications. The extensive use of these catalysts is hindered by issues such as restricted stability, dependence on scarce or hazardous metals, and the intricacy of the molecular pathways that dictate catalytic efficacy. Ongoing investigation of the core processes of organometallic catalysis, bolstered by advanced analytical methods and computational resources, is crucial for overcoming these obstacles and facilitating systematic catalyst advancement. Moreover, integrating catalytic breakthroughs with industrial demands, such as scalability, cost efficiency, and environmental compliance, is essential for converting laboratory achievements into practical applications. Future innovations likely concentrate on the design of catalysts utilizing earth-abundant metals, creation of recyclable catalytic systems, and use of green solvents and continuous-flow technologies. The chemical industry is increasingly emphasizing sustainability, and green catalysis utilizing organometallic complexes is pivotal for the development of cleaner, safer, and more economically feasible production processes.

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Conflict of Interest

Authors have declared that there is no conflict of interest exists.

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framework for studying outcomes in industrial

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