Sustainable Catalysis with Platinum Group Metals: An Interdisciplinary Framework for Ligand Innovation and Green Chemistry Metrics

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ABSTRACT

The transition toward sustainable chemical manufacturing demands interdisciplinary approaches that integrate molecular design and environmental science. This review presents a holistic framework for evaluating platinum group metal (PGM) catalysts, specifically rhodium, palladium, and iridium complexes with hemilabile chalcogen-functionalized phosphine and nitrogen-donor ligands through the lens of green chemistry principles and sustainable catalysis. We examine how ligand hemilability contributes to catalyst longevity and recyclability, analyze life-cycle considerations of PGM utilization from mining to recovery and evaluate emerging catalytic methodologies that minimize waste and energy consumption. Drawing connections between coordination chemistry and industrial process, we assess the environmental footprint of carbonylation, hydroformylation, and cross-coupling processes relative to traditional synthetic routes. The review further explores innovative strategies for catalyst immobilization, electrochemical activation, and photochemical energy transfer that align with United Nations Sustainable Development Goals. By synthesizing perspectives from chemistry, engineering and environmental policy, we propose actionable strategies for reducing the environmental impact of PGM-catalyzed processes while maintaining economic competitiveness.

Keywords: Sustainable catalysis; Green chemistry; Platinum group metals; Hemilabile ligands; Electrocatalysis and Photocatalysis

INTRODUCTION

The Sustainability Imperative in Catalysis

The global chemical industry faces an unprecedented challenge: to maintain production capacity exceeding $5 trillion annually while reducing greenhouse gas emissions, minimizing hazardous waste, and transitioning toward circular resource flows [1]. Catalysis lies at the heart of this transformation, with approximately 90% of all chemical processes employing catalysts at some stage [2]. Among these, platinum group metal (PGM) catalysts occupy a important position to enable some of the most atom-efficient and selective transformations known yet their production leads to significant environmental costs including energy-intensive mining and substantial carbon footprints [3].

The concept of "green catalysis" extends beyond mere reaction efficiency to encompass the entire value chain: feedstock origin, catalyst synthesis, process conditions, product separation, catalyst recovery, and end-of-life disposal [4]. The twelve principles of green chemistry articulated by Anastas and Warner provide a standard framework for evaluating catalytic systems, emphasizing atom economy, reduced toxicity and design for degradation [5]. However, applying these principles to PGM catalysis requires interdisciplinary engagement with materials science, environmental engineering, and industrial ecology.

This review adopts a systems-level perspective on PGM catalysis with hemilabile chalcogen-functionalized phosphine (P–O, P–S, P–Se) and nitrogen-donor ligands. Rather than focusing exclusively on reaction

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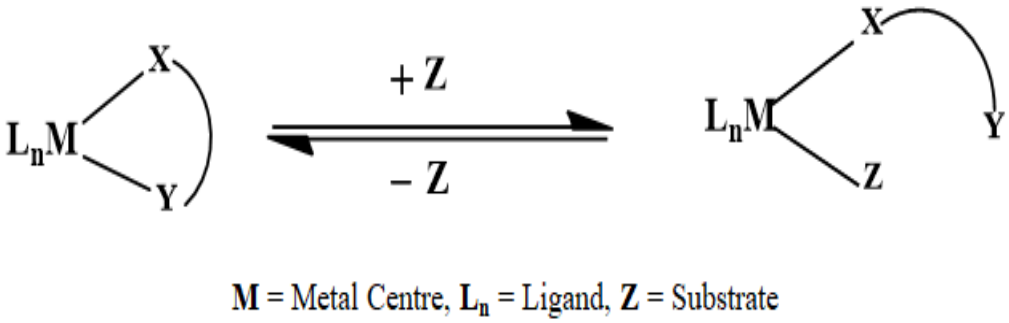
mechanisms or turnover frequencies, we examine how ligand design influences sustainability metrics across multiple dimensions: (i) catalytic efficiency and selectivity (atom economy, E-factor); (ii) catalyst durability and recyclability (turnover number, metal leaching); (iii) process intensification (energy consumption, solvent usage); and (iv) end-of-life management (metal recovery, ligand biodegradability). By integrating these perspectives, we aim to advance a research agenda that positions PGM catalysis as a contributor to, rather than a barrier against, sustainable development.

Theoretical Foundations: Hemilability and Catalytic Sustainability

Coordination Dynamics and Catalyst Longevity

Hemilabile ligands are characterized by the reversible dissociation of a weakly bound donor atom while the primary donor remains coordinated to offer a molecular mechanism for enhancing catalyst longevity [6]. In conventional catalysis, complete ligand dissociation often precedes catalyst decomposition pathways: metal agglomeration, precipitation or formation of catalytically inert clusters. The chelate effect of hemilabile systems suppresses these pathways by maintaining the metal within the ligand coordination sphere even during the catalytically active open form [7].



Scheme 1. Reversible dissociation of hemilabile ligands.

The thermodynamics of hemilability can be understood through the HSAB principle. "Soft" phosphorus donors form strong, covalent bonds with low-valent PGM centers, while "hard" oxygen or intermediate "soft" sulfur/selenium donors coordinate more weakly [8]. The resulting equilibrium between η^2-chelated and η^1-monodentate forms creates a self-regulating system: under substrate-rich conditions, the weak M–X bond dissociates to generate vacant sites; under substrate-depleted conditions, rechelation protects the metal center [9]. This dynamic behavior inherently aligns with green chemistry principles by reducing the stoichiometric excess of ligand required to maintain catalyst stability.

Spectroscopic Probes and Molecular-Level Understanding

Infrared spectroscopy of coordinated carbonyl ligands provides a quantitative window into the electronic effects of hemilabile ligands [10]. The CO stretching frequency reports on metal electron density: electron-rich centers engage in stronger backbonding, lowering ν(CO). Comparative studies reveal that phosphine sulfides and selenides are weaker net donors than parent phosphines, as evidenced by higher CO frequencies in analogous complexes [11]. This electronic attenuation has practical implications for catalytic cycles where oxidative addition (favored by electron richness) and migratory insertion (potentially hindered by strong metal–acyl bonds) must be balanced.

Advanced spectroscopic techniques—including time-resolved IR, stopped-flow UV-Vis, and rapid-injection NMR—have begun to elucidate the kinetics of hemilabile bond dissociation under catalytically relevant conditions [12]. These methods are essential for validating theoretical models and guiding ligand optimization beyond empirical screening.

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Life-Cycle Perspectives on Pgm Utilization

Mining, Refining, and Supply Chain Considerations

PGMs are among the rarest elements in the Earth's crust, with abundances ranging from 0.001 to 0.0001 ppm [13]. Primary production is concentrated in South Africa and Russia, creating supply vulnerabilities and significant environmental impacts from deep underground mining, ore processing, and smelting. Life-cycle assessments indicate that the production of 1 kg of refined rhodium generates approximately 15–20 tonnes of CO_2-equivalent emissions and substantial quantities of sulfur dioxide and particulate matter [14].

These environmental costs amplify the importance of maximizing catalyst productivity. A homogeneous catalyst with a turnover number (TON) of 10^6 effectively distributes the embodied energy and emissions of metal production across 10^6 product molecules, rendering the metal's environmental contribution negligible on a per-mole basis. Conversely, catalysts with low TONs or poor recyclability impose disproportionate environmental burdens. Hemilabile ligands, by enhancing catalyst stability and suppressing decomposition, directly contribute to higher effective TONs and reduced metal consumption.

Catalyst Recovery and Circular Economy Integration

The circular economy framework i.e. eliminating waste through continuous material cycling has gained importance in the chemical industry as a framework for sustainable resource management [15]. For PGM catalysis, circularity requires efficient recovery and reprocessing of spent catalysts, which currently accounts for approximately 40% of global PGM supply [16].

Homogeneous catalysts present unique recovery challenges relative to heterogeneous systems. The molecular dispersion of metal complexes in solution complicates separation from product streams, often necessitating energy-intensive distillation or precipitation steps. Biphasic catalysis, as exemplified by the Ruhrchemie/Rhône-Poulenc hydroformylation process employing water-soluble rhodium–tppts catalysts, enables facile phase separation and catalyst recycling [17]. Hemilabile ligands offer complementary strategies: the chelate effect reduces metal leaching into product phases, while the dynamic coordination behavior may facilitate catalyst regeneration through simple thermal or chemical treatment.

Emerging technologies for PGM recovery from homogeneous systems include supported ionic liquid phases (SILPs), membrane separation, and magnetic nanoparticle immobilization [18]. Each approach must balance catalyst activity (often reduced in constrained environments) against recovery efficiency and operational simplicity.

Green Chemistry Metrics for Pgm-Catalyzed Processes

Atom Economy and E-Factor Analysis

Atom economy, defined as the molecular weight of the desired product divided by the total molecular weight of all reactants, provides a theoretical upper bound on material efficiency [19]. PGM-catalyzed transformations such as hydroformylation (atom economy = 100%, all atoms incorporated) and Suzuki coupling (atom economy limited by stoichiometric base and boron byproducts) compare favorably with classical stoichiometric routes.

The E-factor i.e. kilograms of waste per kilogram of product offers a more pragmatic metric that includes solvents, auxiliaries, and catalyst residues [20]. Pharmaceutical manufacturing typically exhibits E-factors of 25–100, while bulk chemicals achieve <1–5 [20]. PGM-catalyzed processes can contribute to lower E-factors through: (i) high selectivity reducing byproduct formation; (ii) mild conditions minimizing energy input; (iii) catalyst recyclability eliminating metal waste streams; and (iv) solvent optimization replacing volatile organic compounds with greener alternatives.

Process Mass Intensity and Carbon Footprint

Process mass intensity (PMI), the total mass of materials used per mass of product, has become a standard metric in the pharmaceutical industry, with targets of <25 for sustainable processes [21]. PGM-catalyzed steps can

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achieve low PMI values when integrated with efficient workup procedures and solvent recovery systems. However, the contribution of catalyst synthesis to overall PMI is often underappreciated: ligand synthesis involving multiple steps, precious metal precursors, and chromatographic purification can substantially inflate the upstream environmental burden.

Carbon footprint analysis must similarly extend beyond the reaction step to encompass the full supply chain. A recent comparative study of acetic acid production routes found that the Cativa iridium process, despite using a precious metal, exhibited lower life-cycle greenhouse gas emissions than ethane oxidative dehydrogenation due to superior atom economy and reduced separation energy [22].

Catalytic Processes Through A Sustainability Lens

Carbonylation: Water Minimization and Energy Efficiency

Acetic acid production via methanol carbonylation illustrates the evolution of PGM catalysis toward sustainability. The Monsanto rhodium process, while revolutionary in its time, operates at high water concentrations (14–15 wt%) to maintain catalyst stability, incurring substantial energy costs for water removal and product purification [23]. The Cativa iridium process reduced water requirements to 4–8 wt% through ruthenium promotion, cutting separation energy by approximately 30% [24].

Ligand-modified systems offer further improvements. The hemilabile P–S ligand $Ph_2PCH_2P(S)Ph_2$ achieves eight-fold higher activity than the Monsanto catalyst, enabling operation at lower catalyst loadings and reduced metal inventory [25]. From a sustainability perspective, this activity enhancement translates directly to lower embodied energy per tonne of product, provided that ligand synthesis costs and stability are managed.

Hydroformylation: Biphasic and Continuous-Flow Innovation

Hydroformylation exemplifies successful industrial implementation of green chemistry principles. The Ruhrchemie/Rhône-Poulenc process, employing water-soluble rhodium–tppts in a biphasic system, eliminates organic solvent usage for catalyst–product separation and achieves rhodium losses below 10^{-9} g per kg of product [26]. This represents a near-ideal realization of green chemistry principles: catalytic efficiency, waste minimization and inherent safety from non-flammable aqueous media.

Continuous-flow processing extends these advantages. Microreactor technology enables precise temperature control, enhanced mass transfer, and integration with in-line analytics [27]. For hydroformylation, flow reactors have demonstrated improved selectivity through rapid heat removal from the exothermic reaction, suppressing isomerization side reactions [28]. Hemilabile ligands may prove particularly suitable for flow applications: the dynamic coordination behavior could adapt to the constrained hydrodynamic environment of microchannels while maintaining the chelate stability required for long operational runs.

Cross-Coupling: Eliminating Hazardous Reagents

The Suzuki–Miyaura and Sonogashira reactions have transformed pharmaceutical synthesis, yet traditional protocols employ stoichiometric bases, organic solvents, and (in Sonogashira) toxic copper co-catalysts [29]. Recent innovations address these limitations:

- **Aqueous Suzuki:** Water-soluble ligands and boronic acid derivatives enable coupling in aqueous media, eliminating organic solvent waste [30].
- **Copper-free Sonogashira:** Strong bases (KO*t*Bu) or N-heterocyclic carbene ligands facilitate direct palladium–alkyne transmetalation, removing copper-induced homocoupling and simplifying purification [31].
- **Electrochemical activation:** Anodic oxidation replaces stoichiometric chemical oxidants in C–H activation variants, dramatically improving atom economy [32].

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Hemilabile P–X ligands could contribute to these greening efforts by enabling lower catalyst loadings (through enhanced stability) and facilitating catalyst recovery (through chelate retention). However, systematic life-cycle comparisons with established ligand classes are needed to validate these hypotheses.

Table 1. Comparison of various key parameters

Parameter	Carbonylation (Methanol → Acetic Acid)	Hydroformylation (Alkene → Aldehyde)	Cross-Coupling (Suzuki–Miyaura / Sonogashira)
Typical Catalyst	Rh (Monsanto), Ir/Ru (Cativa), ligand-modified Rh/Ir	Rh–TPPTS, Rh–phosphine, Rh–hemilabile ligands	Pd–phosphine, Pd–NHC, Pd–hemilabile ligands
Industrial Maturity	Fully commercial	Fully commercial	Commercial (fine chemicals, pharmaceuticals)
Catalyst Activity (TOF)	Up to ~8× Monsanto with hemilabile ligands	High (10^3–10^5 h^{-1} depending on substrate)	Moderate–high (10^2–10^5 turnovers)
Catalyst Recovery	High (>99% metal retained industrially)	Excellent in biphasic systems	Variable; often limited in homogeneous systems
Role of Hemilabile Ligands	Increase activity, reduce catalyst loading and energy demand	Improve catalyst stability and long-term operation under flow	Lower Pd loading, improve stability and facilitate recycling
Primary Sustainability Challenge	High water demand and separation energy	Catalyst recovery and syngas utilisation	Solvent consumption, catalyst recovery, base waste

Emerging Methodologies: Electrochemistry And Photocatalysis

Electrochemical C–H Activation

The merger of transition metal catalysis with electrochemistry, termed metalla-electrocatalysis represents one of the most promising avenues for sustainable synthesis [32]. By replacing stoichiometric chemical oxidants with anodic electron transfer, these methods eliminate hazardous waste generation and enable precise control over oxidation potential.

Rhodium-catalyzed electrochemical C–H activation has demonstrated remarkable versatility. Rh(III)-catalyzed directed C–H functionalization of arenes with alkenes, alkynes, and diazo compounds proceeds under constant current conditions with ferrocene or iodide mediators, achieving turnovers comparable to chemical oxidation protocols. The electrochemical approach offers particular advantages for oxidative coupling reactions, where traditional methods require superstoichiometric amounts of Ag(I), Cu(II), or peroxides.

From a sustainability perspective, electrochemical methods align with renewable energy integration: when powered by solar or wind electricity, the carbon footprint of synthesis approaches zero at the point of use. However, challenges remain in scaling electrochemical reactors, managing electrode fouling, and ensuring competitive space-time yields relative to thermochemical processes.

Photochemical Energy Transfer

Visible-light photocatalysis has emerged as a complementary strategy for activating PGM catalysts under mild conditions [33]. For instance photoexcited iridium (III) polypyridyl complexes can engage in single-electron transfer or energy transfer with substrates, enabling transformations inaccessible through thermal activation alone.

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The integration of hemilabile ligands with photocatalytic systems is largely unexplored but conceptually attractive. The dynamic coordination environment could facilitate photoinduced ligand exchange, generating reactive intermediates upon light absorption while protecting the metal center in the dark state. Such "photoswitchable" catalysts would offer temporal control over reactivity, reducing unwanted side reactions during workup and storage.

Toxicological And Regulatory Considerations

PGM Exposure and Environmental Fate

While PGM complexes are generally handled in closed industrial systems, environmental releases occur through automotive catalytic converter wear, hospital wastewater (from platinum anticancer drugs), and improper disposal of electronic waste [34]. Once in the environment, PGMs can undergo speciation transformations—oxidation, complexation with natural organic matter, or bioaccumulation that alter their toxicity profiles.

The toxicology of PGM compounds varies dramatically with oxidation state and ligand environment. Soluble Pt(II) complexes (e.g., cisplatin) may exhibit gene toxicity through DNA crosslinking, while insoluble Pt(0) metal is comparatively inert [35]. Rhodium and iridium compounds have received less toxicological scrutiny, though occupational exposure limits have been established for metal dusts and salts.

Regulatory Frameworks and Industry Compliance

Chemical regulation increasingly emphasizes hazard reduction and transparency. The European Union's REACH legislation requires registration and risk assessment of all chemicals produced or imported in quantities exceeding 1 tonne per annum [36]. For PGM catalysts, this necessitates comprehensive toxicological data and exposure assessments that can be prohibitively expensive for novel ligand systems.

Green chemistry certification schemes, such as the EPA's Safer Choice program and the EU Ecolabel, provide market incentives for sustainable formulations [37]. Catalyst systems that demonstrably reduce hazard—through lower metal content, biodegradable ligands or aqueous processing may gain competitive advantage in regulated markets.

Integrating Computational Design with Environmental Assessment

The future of sustainable PGM catalysis lies at the intersection of molecular modeling, process simulation, and life-cycle assessment. Density functional theory (DFT) calculations can predict ligand effects on catalytic cycles, while machine learning algorithms trained on experimental databases can identify structure–activity relationships across diverse chemical spaces [38]. Concurrently, process simulation tools (Aspen Plus, gPROMS) enable evaluation of energy and mass flows at the reactor and plant scale.

The critical gap lies in connecting these scales: translating molecular-level predictions into macroscopic sustainability metrics. Emerging frameworks for "molecular systems engineering" aim to bridge this divide by parameterizing DFT-derived descriptors for input into process models [39].

CONCLUSIONS

Platinum group metal catalysis with hemilabile ligands occupies a unique position at the nexus of molecular innovation and sustainable development. The dynamic coordination chemistry of P–O, P–S, P–Se, and N-donor systems offers mechanisms for enhancing catalyst longevity, selectivity and recyclability attributes that directly translate into reduced environmental impact and improved economic viability.

However, realizing the full sustainability potential of these catalysts requires transcending traditional disciplinary boundaries. Chemists must engage with life-cycle assessment methodologies to quantify environmental footprints; engineers must develop processes that integrate catalyst recovery and renewable energy; and policymakers must create regulatory frameworks that incentivize green innovation without stifling technological development.

The path forward demands not merely more efficient catalysts, but catalysts designed for sustainability from the molecular level upward. By embedding green chemistry principles into ligand design, process development and end-of-life planning, the field can ensure that PGM catalysis contributes meaningfully to a circular, low-carbon chemical industry.

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