# Hemilabile Ligand Architectures in Platinum Group Metal Catalysis: Structure–Activity Relationships and Process Engineering Perspectives

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## ABSTRACT

The rational design of hemilabile ligand frameworks has emerged as a pivotal strategy for modulating the catalytic performance of platinum group metal (PGM) complexes in homogeneous catalysis. This review examines the coordination chemistry and catalytic applications of rhodium, palladium, and iridium complexes bearing chalcogen-functionalized phosphine (P–O, P–S, P–Se) and nitrogen-donor ligands, with particular emphasis on structure–activity relationships that govern industrial processes. We analyze how the differential donor strengths of "hard" oxygen versus "soft" sulfur/selenium atoms within heterobidentate frameworks enable dynamic site generation through reversible M–X bond dissociation, and how this hemilability translates into enhanced turnover frequencies in carbonylation, hydroformylation, and cross-coupling reactions. Critical evaluation of landmark systems—including the Monsanto and Cativa acetic acid processes, rhodium-catalyzed hydroformylation generations, and palladium-mediated Suzuki–Sonogashira couplings—reveals the interplay between ligand bite angle, electronic tuning, and steric congestion in optimizing catalytic cycles. The review further addresses current challenges in scaling laboratory catalysts to continuous-flow industrial operations, with perspectives on ligand degradation pathways and catalyst recovery strategies. By bridging molecular-level coordination chemistry with reactor engineering principles, this work provides a mechanistic foundation for the next generation of PGM catalysts in sustainable chemical manufacturing.

**Keywords:** Hemilabile ligands; Platinum group metals; Structure–activity relationships; Homogeneous catalysis; Process engineering; Carbonylation; Hydroformylation

## INTRODUCTION

Homogeneous catalysis by transition metal complexes underpins a substantial fraction of global chemical manufacturing, with platinum group metal (PGM) catalysts alone accounting for processes generating tens of millions of tonnes of chemicals annually [1]. The ability to fine-tune catalyst performance through ligand design distinguishes homogeneous from heterogeneous systems, enabling precise control over regioselectivity, stereoselectivity, and activity under mild conditions [2]. Among the arsenal of ligand architectures, hemilabile heterobidentate systems—combining a strongly bound primary donor with a weakly coordinated secondary donor, have attracted sustained attention for their capacity to stabilize catalytic intermediates while transiently generating vacant coordination sites for substrate binding [3].

The conceptual foundation of hemilability rests on the Hard–Soft Acid–Base (HSAB) principle articulated by Pearson [4]. In PGM complexes, "soft" phosphine donors (P) form robust bonds with low-valent metal centers through effective σ-donation and dπ–σ* backbonding, whereas "hard" oxygen or intermediate "soft" sulfur/selenium donors (X) coordinate more weakly, rendering the M–X bond susceptible to reversible cleavage [5]. This differential lability engenders a dynamic equilibrium between $\eta^2$-chelated and $\eta^1$-monodentate coordination modes, effectively switching the metal center between coordinatively saturated (stable) and unsaturated (reactive) states without requiring complete ligand dissociation [6].

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This review focuses specifically on the structure–activity relationships of rhodium, palladium, and iridium complexes bearing P–O, P–S, P–Se, and N-donor hemilabile ligands. Rather than presenting a comprehensive survey, we critically evaluate how ligand parameters i.e. bite angle, donor strength, backbone flexibility and steric bulk translate into measurable catalytic outcomes in industrially relevant transformations. By examining carbonylation, hydroformylation and carbon–carbon coupling processes through a mechanistic lens, we aim to establish design principles that guide the development of more robust, selective and economically viable PGM catalysts.

## Ligand Design Parameters And Coordination Chemistry

### Electronic Tuning Through Chalcogen Functionalization

The functionalization of tertiary phosphines with chalcogen atoms (O, S, Se) generates phosphine oxides ($R_3P{=}O$), sulfides ($R_3P{=}S$), and selenides ($R_3P{=}Se$), each imparting distinct electronic characteristics to the resulting metal complexes [7]. Oxygen, as a hard donor with no low-energy d-orbitals, engages in primarily ionic M–O interactions that stabilize higher oxidation states; conversely, sulfur and selenium, being softer and more polarizable, form more covalent yet comparatively labile M–S/Se bonds [8].

The electronic consequences of these bonding differences can be quantified through infrared spectroscopic analysis of coordinated carbonyl ligands. Carbon monoxide functions as a sensitive probe of metal electron density: strong σ-donating ligands increase electron richness at the metal center, enhancing $d\pi \rightarrow \pi^*$ backbonding to CO and concomitantly lowering ν(CO) [9]. Comparative studies of [RhCl(CO)L] complexes (L = phosphine versus phosphine chalcogenide) have established that phosphine sulfides and selenides are weaker net electron donors than their parent phosphines, as evidenced by elevated CO stretching frequencies relative to analogous triphenylphosphine complexes [10].

Beyond single-donor systems, heterobidentate P–X ligands introduce an additional layer of electronic complexity. The chelate effect stabilizes the $\eta^2$-coordination mode, yet the weaker M–X interaction remains poised for dissociation under thermal or substrate-induced stimulus. This behavior has been documented extensively for P–O systems; for instance, the keto-phosphine ligand $Ph_2PCH_2COOEt$ forms fac-$[RhCl_3(Ph_2PCH_2COOEt)(Ph_2PCH_2COOEt)]$ with $RhCl_3 \cdot 3H_2O$, wherein both chelated and dangling phosphine environments coexist in dynamic equilibrium [11]. Variable-temperature $^{31}P$ NMR spectroscopy reveals rapid site exchange at ambient temperature, freezing into distinct resonances only below −2 °C, confirming the lability of the Rh–O interaction [11].

### Steric Factors and Bite Angle Effects

While electronic effects govern the thermodynamics of metal–ligand bonding, steric parameters dictate the kinetics of substrate approach and the geometry of catalytic transition states. The bite angle i.e. the P–M–X angle in chelated complexes emerges as a critical descriptor, influencing both the stability of the chelate ring and the accessibility of coordination sites [12].

Diphosphine ligands with methylene spacers ($Ph_2P(CH_2)_nP(O)Ph_2$; n = 1, 2) have been systematically investigated in rhodium carbonyl chemistry. The n = 2 derivative forms a six-membered chelate with Rh(I), exhibiting pronounced hemilability: the Rh–O bond dissociates reversibly upon CO coordination to generate the catalytically active dicarbonyl species [13]. In contrast, analogous P–S ligands such as $Ph_2PCH_2P(S)Ph_2$ form more rigid five-membered chelates where the M–S bond remains intact under comparable conditions, suggesting that both bite angle and donor identity modulate hemilability [14].

Sterically demanding ligands introduce further complexity. Grushin's studies on bis-phosphine monoxides with palladium(II) revealed that bulky substituents initially enforce bidentate coordination to minimize steric clash [15]. However, upon addition of excess ligand or substrate, the steric congestion drives reversible Pd–O bond dissociation, effectively converting the catalyst from a coordinatively saturated resting state to a reactive monodentate form [15]. This ligand-induced self-regulation represents an elegant mechanism for controlling catalyst speciation without external stimulus.

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## Rhodium Catalysis: Carbonylation And Hydroformylation

### Methanol Carbonylation: From Monsanto to Ligand-Accelerated Systems

Acetic acid production via methanol carbonylation stands as one of the most economically significant applications of homogeneous catalysis, with global capacity exceeding 15 million tonnes per annum [16]. The Monsanto process, commercialized in the 1970s, employs a rhodium(I) iodide catalyst operating at 150–200 °C and 30–60 atm CO, achieving selectivity exceeding 99% [17]. The active catalytic species, $[Rh(CO)_2I_2]^-$, cycles through oxidative addition of methyl iodide, migratory insertion of CO, and reductive elimination of acetyl iodide, which subsequently hydrolyzes to acetic acid [17].

Despite its industrial success, the Monsanto system exhibits limitations: rhodium loss through precipitation in the high-water regime (14–15 wt%) and substantial energy costs associated with product separation from the aqueous phase [18]. These drawbacks motivated the development of iridium-based Cativa technology and, concurrently, ligand-modified rhodium systems that operate under reduced water concentrations.

The introduction of hemilabile P–O and P–S ligands has yielded catalysts with markedly enhanced activity. Wegman and coworkers demonstrated that cis-$[RhCl(CO)(\eta^2\text{-}Ph_2PCH_2CH_2P(O)Ph_2)]$ serves as a highly active carbonylation precursor, undergoing reversible phosphine oxide dissociation to generate the coordinatively unsaturated dicarbonyl intermediate required for methyl iodide oxidative addition [13]. Remarkably, Baker and colleagues reported that the P–S ligand $Ph_2PCH_2P(S)Ph_2$ confers even greater activity: the complex cis-$[Rh(CO)Cl(\eta^2\text{-}Ph_2PCH_2P(S)Ph_2)]$ exhibits approximately eight-fold higher turnover frequency than the Monsanto catalyst [14].

Mechanistic investigations by Gonsalvi and coworkers elucidated the origins of this enhanced activity [19]. While electron-donating ligands typically accelerate oxidative addition (by increasing metal electron density) while retarding migratory insertion (by strengthening the Rh–acyl bond through enhanced backbonding), the $Ph_2PCH_2P(S)Ph_2$ system circumvents this trade-off. X-ray crystallographic analysis of the acyl intermediate $[Rh(COCH_3)I_2(\eta^2\text{-}Ph_2PCH_2P(S)Ph_2)]$ revealed that the phenyl rings are oriented to create substantial steric congestion around the metal center [19]. This steric pressure accelerates migratory insertion by destabilizing the acyl complex and promoting CO insertion into the $Rh–CH_3$ bond. Thus, the ligand simultaneously enhances both key steps of the catalytic cycle through a combination of electronic (P-donor) and steric (phenyl orientation) effects, a synergistic outcome unattainable with monodentate phosphines.

### Hydroformylation: Generational Advances in Ligand Design

Hydroformylation is the addition of a formyl group and hydrogen across an alkene double bond which ranks among the largest-scale applications of homogeneous catalysis, with global aldehyde production exceeding 10 million tonnes annually [20]. The reaction's industrial importance stems from the versatility of aldehyde products, which serve as precursors to alcohols, carboxylic acids, esters and plasticizers.

First-generation cobalt catalysts (1938, Roelen) utilized $Co_2(CO)_8$, which undergoes hydrogenolysis to the active catalyst $HCo(CO)_4$ [20]. These systems required harsh conditions (150–200 °C, 200–300 atm) and suffered from poor selectivity, generating mixtures of linear and branched aldehydes along with alcohol byproducts.

Second-generation rhodium catalysts (mid-1970s) represented a paradigm shift. Rhodium complexes modified with triphenylphosphine (Celanese, 1974; Union Carbide, 1976; Mitsubishi, 1978) operated under milder conditions (50–120 °C, 10–50 atm) with superior linear-to-branched (l:b) ratios [21]. The enhanced activity derives from rhodium's greater propensity for oxidative addition and its higher natural abundance of reactive low-coordinate intermediates.

Third-generation biphasic systems (Ruhrchemie/Rhône-Poulenc, 1984) addressed catalyst–product separation by employing the water-soluble ligand tppts (triphenylphosphine trisulfonate sodium salt) [22]. The rhodium–

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tppts catalyst resides in an aqueous phase, while the butanal product partitions into the organic phase, enabling continuous operation with minimal rhodium loss.

Recent advances have focused on phosphite and hemilabile diphosphine ligands. Van Leeuwen's discovery that bulky monophosphites achieve exceptionally high reaction rates, surpassing triphenylphosphine by orders of magnitude, where the steric bulk accelerates the rate-determining alkene insertion step while suppressing hydrogenation side reactions [23]. Diphosphines with wide bite angles (>110°) favor equatorial–apical coordination in trigonal bipyramidal rhodium hydridoalkyl intermediates, directing regioselectivity toward linear aldehydes [24].

Hemilabile P–O ligands offer a promising avenue for next-generation hydroformylation catalysts. The reversible dissociation of the weak M–O bond could, in principle, generate the coordinatively unsaturated species required for alkene binding without necessitating complete ligand dissociation. This would combine the high activity characteristic of monodentate phosphine systems with the thermal stability and selectivity benefits of chelating architectures. However, realizing this potential requires precise tuning of the P–O bond strength: too strong and the catalyst remains coordinatively saturated; too weak and the ligand dissociates irreversibly, leading to catalyst decomposition.

## Palladium Catalysis: Carbon–Carbon Bond Formation

### Suzuki–Miyaura Coupling: Ligand Effects on Turnover Efficiency

The Suzuki–Miyaura reaction—the palladium-catalyzed cross-coupling of organoboron reagents with organic halides—has become a cornerstone of pharmaceutical and materials synthesis, recognized with the 2010 Nobel Prize in Chemistry [25]. The catalytic cycle comprises three fundamental steps: oxidative addition of Pd(0) to the aryl halide, transmetalation of the boron-ate complex with the resulting Pd(II) species, and reductive elimination to forge the C–C bond [26].

Ligand design has been instrumental in expanding the reaction scope to include previously challenging substrates. Bulky, electron-rich monophosphines such as P*t*Bu$_3$ and Q-phos achieve remarkable turnover numbers (>$10^6$) by stabilizing monoligated Pd(0) intermediates that undergo rapid oxidative addition to aryl chlorides [27]. The steric bulk of these ligands favors the formation of reactive LPd(0) species over less active $L_2$Pd(0) complexes, effectively increasing the concentration of the catalytically competent form.

Hemilabile P–S and P–Se ligands present an underexplored opportunity in Suzuki catalysis. The "soft" sulfur or selenium donor could stabilize the Pd(0) oxidation state through π-backbonding, while reversible dissociation would generate the coordinative unsaturation required for substrate approach. Preliminary studies on palladium complexes of phosphinothioethers (e.g., $Ph_2PCH_2SCH_3$) have demonstrated activity in related carbonylation and arylation processes [28], suggesting that systematic optimization of bite angle and donor strength could yield competitive Suzuki catalysts.

### Sonogashira Coupling and Copper-Free Variants

The Sonogashira reaction couples terminal alkynes with vinyl or aryl halides to generate conjugated enynes and aryl alkynes—structural motifs prevalent in natural products, pharmaceuticals, and optoelectronic materials [29]. Traditional protocols employ a palladium catalyst, CuI co-catalyst, and amine base, with the copper functioning to transmetalate the terminal alkyne to a copper acetylide that subsequently transfers to palladium [30].

The copper co-catalyst, while mechanistically beneficial, introduces practical limitations: it promotes Glaser-type homocoupling of the alkyne, complicates product purification, and is incompatible with substrates bearing oxidatively sensitive functional groups [31]. These drawbacks have motivated extensive research into copper-free Sonogashira variants, typically employing strong bases (e.g., *t*-BuOK) or specialized ligand systems that enable direct palladium–alkyne interaction.

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Phosphine ligands such as $PtBu_3$, $PCy_3$, and N-heterocyclic carbenes have proven effective in copper-free protocols [32]. The development of hemilabile P–X ligands for this transformation remains nascent but theoretically attractive: the weakly bound X donor could stabilize the Pd(0) resting state while dissociating to accommodate the alkyne during the catalytic cycle. Future studies should evaluate whether P–S or P–Se hemilability can supplant the copper transmetalation pathway by facilitating direct alkyne coordination to palladium.

## Iridium Catalysis: Hydrogenation And Beyond

### Vaska's Complex and Crabtree's Catalyst: Foundations of Iridium Reactivity

Iridium's prominence in homogeneous catalysis rests on two iconic complexes. Vaska's complex, trans-$[IrCl(CO)(PPh_3)_2]$, was the first transition metal compound demonstrated to bind molecular oxygen reversibly—a landmark discovery that illuminated the electronic factors governing dioxygen activation [33]. Crabtree's catalyst, $[Ir(COD)(PCy_3)(Py)]^+PF_6^-$, achieves exceptional activity in alkene hydrogenation, including substrates that resist reduction by other catalysts [34]. Both complexes share a square-planar $d^8$ configuration with 16 valence electrons, and their reactivity toward small molecules ($H_2$, $O_2$, CO, RX) stems from this coordinative unsaturation.

The development of phosphine chalcogenide analogues has extended the structural diversity of iridium catalysts. Complexes $[Ir(COD)ClL]$ (L = $Me_3PS$, $Me_2PhPS$, $MePh_2PS$) and Ir(COD)L (L = $dpmS_2$, $dpmSe_2$) demonstrate that sulfur and selenium donors can support the Ir(I) oxidation state while introducing hemilabile character [35]. The square-planar iridium(I) centers in these complexes undergo oxidative addition with HCl, $I_2$, and $CH_3I$, generating octahedral iridium(III) products that can participate in catalytic cycles.

### The Cativa Process and Ligand-Promoted Iridium Carbonylation

The Cativa process, commercialized by BP Chemicals in 1996, represents the most significant industrial application of iridium homogeneous catalysis [36]. Operating with an iridium–iodide catalyst promoted by ruthenium or other metal carbonyls, the process achieves methanol carbonylation at lower water concentrations (4–8 wt%) than the Monsanto technology, reducing downstream separation costs and suppressing the water–gas shift reaction [36].

Subsequent research has demonstrated that the iridium system can be further enhanced by ligand modification. Ruthenium promotion is understood to facilitate iodide abstraction from $[Ir(CO)_2I_3Me]^-$, generating the neutral $[Ir(CO)_2I_2Me]$ species that undergoes rapid migratory insertion [37]. The application of hemilabile P–O or P–S ligands to iridium carbonylation has received limited attention but presents intriguing possibilities: ligands that accelerate iodide dissociation while stabilizing the Ir(I) resting state could, in principle, combine the water efficiency of Cativa with the activity of ligand-modified rhodium systems.

### Comparison of PGM Catalysts with Earth-Abundant Metal Alternatives

Although platinum group metals remain the benchmark for many homogeneous catalytic transformations because of their exceptional activity, selectivity, and functional-group tolerance, increasing concerns regarding cost, limited natural abundance, and supply-chain vulnerability have stimulated considerable interest in catalysts based on earth-abundant metals such as iron, cobalt, nickel, copper and manganese. These first-row transition metals offer significant sustainability advantages owing to their higher crustal abundance, lower toxicity and substantially reduced cost.

In carbonylation and hydroformylation, rhodium and iridium catalysts continue to outperform earth-abundant analogues in terms of turnover frequency (TOF), catalyst lifetime, and product selectivity under industrial conditions. Nevertheless, cobalt-based hydroformylation catalysts remain commercially relevant and recent ligand-engineering strategies have significantly improved their activity under milder operating conditions. Similarly, iron- and cobalt-based catalysts have demonstrated encouraging performance in hydrogenation and

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C–H functionalization reactions, although catalyst stability and substrate scope remain inferior to those of PGM systems.

In palladium-catalyzed cross-coupling chemistry, nickel has emerged as one of the most promising sustainable alternatives because of its ability to activate aryl chlorides and catalyse a wide range of C–C bond-forming reactions. However, nickel catalysts frequently exhibit lower functional-group tolerance, greater sensitivity to air and moisture, and increased susceptibility to competing radical pathways compared with palladium complexes [38].

Consequently, future development of hemilabile ligand systems should not be restricted to platinum-group metals alone. Applying the design principles established for PGM complexes to earth-abundant metals may provide catalysts that combine acceptable catalytic performance with improved economic and environmental sustainability.

**C–H Activation: Emerging Frontiers**

Direct functionalization of C–H bonds represents a transformative approach to molecular synthesis, eliminating the need for pre-functionalized starting materials and aligning with principles of atom economy and step efficiency [39]. Rhodium and palladium catalysts have been at the forefront of this field, with recent advances extending from ortho-directed activation to remote meta- and para-selective transformations.

Rhodium(III)-catalyzed C–H activation has matured into a powerful synthetic platform. Directed functionalization of 2-phenylpyridines and related substrates enables C–C, C–N, and C–O bond formation under oxidative conditions, with the rhodium center cycling between Rh(I) and Rh(III) oxidation states [40]. Recent developments include electrochemical variants that replace stoichiometric chemical oxidants with anodic oxidation, significantly improving the sustainability profile of these transformations [41].

Palladium-catalyzed C–H activation has similarly evolved. The α-arylation of ketones, concurrently reported by Miura, Buchwald, and Hartwig, demonstrates how ligand sterics control selectivity: bulky bidentate ligands (dtpf, BINAP) inhibit β-hydride elimination from palladium-alkyl intermediates, favoring reductive elimination to the arylated product [42]. The directing group strategy has been extended to meta-selective C–H functionalization through U-shaped templates or norbornene-mediated relay catalysis, enabling functionalization at positions previously inaccessible [43].

The application of hemilabile P–X ligands to C–H activation remains largely unexplored. Theoretical considerations suggest that ligands combining a strongly bound P-donor with a weakly coordinated O-, S-, or N-donor could stabilize the high oxidation state Pd(II) or Rh(III) intermediates required for C–H cleavage while transiently dissociating to accommodate the coupling partner. This represents a promising direction for future ligand design.

**Process Engineering And Industrial Translation**

**Catalyst Stability and Degradation Pathways**

The translation of laboratory catalysts to industrial processes requires addressing stability under process conditions. PGM catalysts face several degradation mechanisms: (i) phosphine oxidation by trace oxygen to phosphine oxides, which alter coordination properties; (ii) P–C bond cleavage at elevated temperature, generating metal phosphides and free arenes; (iii) metal agglomeration and precipitation, particularly in low-ligand-concentration regimes [44].

Hemilabile ligands present both advantages and challenges in this context. The chelate effect suppresses complete ligand dissociation, reducing metal loss through precipitation. However, the weak M–X bond may be susceptible to protolysis or nucleophilic attack by reaction components (water, alcohols, carboxylic acids), potentially leading to catalyst deactivation. Understanding these degradation pathways is essential for designing ligands that balance hemilability with hydrolytic and thermal stability. A comparison of various PGM catalysts with various metals is shown in Table 1.

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Future investigations should also evaluate catalyst durability using standardized performance metrics, including turnover number (TON), turnover frequency (TOF), product selectivity, catalyst lifetime, recyclability and resistance to metal leaching. Direct comparison of these parameters across PGM and earth-abundant metal catalysts would facilitate objective assessment of catalyst efficiency and sustainability while providing valuable benchmarks for industrial implementation.

Table 1. Comparison of various PGM metal catalysts

| Catalyst System | Activity (TOF) | Selectivity | Stability | Recyclability | Sustainability |
|---|---|---|---|---|---|
| Rh-based PGM | Excellent | Excellent | Excellent | Moderate | High performance but expensive |
| Ir-based PGM | Excellent | Excellent | Excellent | Moderate | Lower water demand but scarce |
| Pd-based PGM | Excellent | Excellent | Good | Moderate | Widely used but costly |
| Fe-based | Moderate | Moderate | Moderate | Good | Excellent sustainability |
| Co-based | Moderate–High | Moderate | Good | Good | Low cost and abundant |
| Ni-based | High (cross-coupling) | Moderate | Moderate | Good | Most promising PGM alternative |

**Continuous-Flow and Biphasic Processing**

Continuous-flow reactor technology offers significant advantages over batch operation for homogeneous catalysis: improved heat and mass transfer, enhanced safety with reactive intermediates, and facile integration with in-line purification [45]. Biphasic systems, exemplified by the Ruhrchemie/Rhône-Poulenc hydroformylation process, enable catalyst–product separation without distillation, minimizing thermal degradation of sensitive ligands [22].

The development of supported ionic liquid phase (SILP) and supported aqueous phase (SAP) catalysts extends the biphasic concept by immobilizing the catalyst on a solid support while maintaining the advantages of homogeneous active sites [46]. Hemilabile ligands could prove particularly advantageous in these systems: the dynamic coordination behavior may adapt to the constrained environment of supported films, maintaining activity while the chelate architecture prevents metal leaching.

An equally important challenge is understanding the long-term behaviour of hemilabile ligands under continuous industrial operation. Although reversible donor coordination is advantageous for catalytic turnover, repeated coordination–dissociation cycles under elevated temperatures, high pressures, and chemically aggressive media may eventually induce ligand degradation, donor oxidation, or irreversible structural rearrangements. Long-duration continuous-flow studies coupled with operando spectroscopic characterization are therefore required to establish catalyst durability and identify degradation mechanisms under realistic manufacturing conditions.

## CONCLUSIONS AND OUTLOOK

Hemilabile chalcogen-functionalized phosphine and nitrogen-donor ligands represent a mature yet still-evolving class of ligand architectures for PGM catalysis. The structure–activity relationships elucidated over the past four decades establish clear design principles: (i) the primary P-donor should be sufficiently electron-donating to promote oxidative addition and stabilize low oxidation states; (ii) the secondary X-donor must be weakly bound enough to dissociate under catalytic conditions yet strong enough to prevent complete ligand loss; (iii) the backbone should enforce a bite angle that balances chelate stability with coordinative flexibility.

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Looking forward, several research directions merit intensified investigation. First, comparative studies between platinum-group metal catalysts and earth-abundant alternatives should be prioritized to identify catalytic systems that balance activity, selectivity, catalyst stability, recyclability, economic viability, and environmental sustainability. Such comparisons should employ standardized catalytic metrics, including turnover number (TON), turnover frequency (TOF), product selectivity, catalyst lifetime, and resistance to deactivation, enabling objective benchmarking across different catalyst platforms.

Second, further investigation into the long-term stability of hemilabile ligands under industrial operating conditions is essential. Continuous-flow reactors, prolonged operation, elevated temperatures, high pressures, and chemically demanding reaction media may significantly influence ligand integrity and catalyst lifetime, yet these aspects remain insufficiently explored.

Third, integrating computational chemistry, density functional theory (DFT), high-throughput virtual screening, and machine-learning methodologies with experimental validation offers a powerful strategy for accelerating ligand discovery. Predictive modelling can identify promising ligand architectures, estimate reaction energetics, and prioritize experimental candidates, thereby reducing the time and resources required for catalyst optimization.

Finally, extending hemilabile ligand design principles to catalysts based on earth-abundant transition metals such as iron, cobalt, nickel, and manganese may provide economically attractive and environmentally sustainable alternatives for future homogeneous catalytic processes.

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