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Exploring transition metal-catalyzed reactions for tailored PAH architectures

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Abstract
Transition metal-catalyzed reactions have emerged as powerful tools for constructing tailored polycyclic aromatic hydrocarbon (PAH) architectures, offering precise control over the formation of carbon-carbon bonds and enabling the synthesis of complex PAH structures with specific shapes, sizes, and functionalities. Palladium, nickel, copper, and ruthenium catalysts facilitate C–C coupling, C–H activation, and annulation processes, allowing for the controlled assembly of extended π-conjugated systems. The versatility of these catalysts enables the incorporation of heteroatoms and functional groups, further expanding the diversity of accessible PAH architectures. Computational studies using density functional theory provide insights into transition state stabilization, ligand effects, and electronic structure modulation, aiding in the rational design of efficient PAH synthesis strategies. Functionalized PAHs synthesized via transition metal catalysis find extensive applications in organic electronics, photovoltaics, energy storage, and bioimaging due to their tunable electronic properties, high charge carrier mobility, and excellent thermal stability. However, challenges remain in terms of reaction scalability, catalyst stability, and the integration of computational predictions with experimental outcomes. Future research should focus on developing sustainable catalytic systems, improving reaction efficiency, and expanding the scope of PAH-based materials for emerging applications in nanotechnology and molecular electronics. By addressing these challenges, transition metal-catalyzed PAH synthesis will continue to drive innovation in the development of advanced functional materials and next-generation electronic devices.

Keywords: Transition metal-catalyzed reactions, polycyclic aromatic hydrocarbons (PAHs), carbon-carbon bond formation, palladium catalysis, nickel catalysis, copper catalysis, ruthenium catalysis, C–H activation, annulation, π-conjugated systems, heteroatom incorporation, density functional theory, organic electronics, photovoltaics, energy storage, bioimaging, nanotechnology, molecular electronics

Introduction

Transition metal-catalyzed reactions have emerged as powerful tools for constructing tailored polycyclic aromatic hydrocarbon (PAH) architectures. These reactions offer precise control over the formation of carbon-carbon bonds, enabling the synthesis of complex PAH structures with specific shapes, sizes, and functionalities. The ability to manipulate these molecular features has opened up new avenues for the design and development of advanced materials with unique properties (Yuan, 2014) [21].

Palladium-catalyzed cross-coupling reactions, such as Suzuki-Miyaura and Stille couplings, have been particularly effective in assembling PAH building blocks. These reactions allow for the controlled formation of carbon-carbon bonds between aryl halides and organometallic reagents, facilitating the stepwise construction of extended π-conjugated systems (Sain *et al*., 2020) [13]. The versatility of palladium catalysts, combined with the wide availability of suitable coupling partners, has made these reactions indispensable tools in PAH synthesis (So & Kwong, 2011) [16].

Additionally, rhodium-catalyzed [2+2+2] cycloadditions have proven valuable for creating curved and strained PAH systems. This elegant transformation enables the simultaneous formation of three new carbon-carbon bonds, resulting in the rapid assembly of benzene rings and other cyclic structures (Tait & Tam, 2018) [17]. The ability to generate curved PAHs is particularly important for the synthesis of bowl-shaped molecules and carbon nanotubes, which have attracted significant interest due to their unique electronic and mechanical properties.

Ruthenium-catalyzed ring-closing metathesis has also emerged as a powerful method for constructing PAH frameworks. This reaction allows for the formation of carbon-carbon double bonds through the rearrangement of alkene precursors, providing access to macrocyclic and polycyclic structures (Fogg & Conrad, 2006) [2]. The high functional group tolerance and mild reaction conditions of ruthenium catalysts make this approach particularly attractive for the synthesis of complex PAH architectures (Alvaro *et al*., 1999) [1].

The versatility of transition metal catalysts allows for the incorporation of heteroatoms and functional groups, further expanding the diversity of accessible PAH architectures. For example, the introduction of nitrogen, oxygen, or sulfur atoms into the PAH framework can significantly alter the electronic properties and reactivity of the resulting molecules. This ability to fine-tune the electronic structure of PAHs is crucial for developing materials with tailored optoelectronic properties. By carefully selecting catalysts, ligands, and reaction conditions, researchers can fine-tune the reactivity and selectivity of these transformations. This level of control enables the synthesis of PAHs with precise molecular structures, including those that would be challenging or impossible to access through traditional synthetic methods. The development of chiral ligands and catalysts has also opened up possibilities for the enantioselective synthesis of chiral PAHs, which have potential applications in asymmetric catalysis and chiral recognition (Glos & Reiser, 2000) [3].

The impact of transition metal-catalyzed reactions on PAH synthesis extends beyond the laboratory, leading to the development of novel PAH-based materials with

applications in various fields. In organic electronics, PAHs serve as active components in organic lightemitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic devices. The ability to precisely control the molecular structure of PAHs allows for the optimization of charge transport properties and energy levels, leading to improved device performance.

In the field of photonics, PAHs with extended π-conjugation exhibit interesting nonlinear optical properties, making them suitable for applications in optical limiting devices and twophoton absorption materials. The structural diversity accessible through transition metalcatalyzed reactions enables the design of PAHs with enhanced nonlinear optical responses (Khattak, 2022) [7].

Nanotechnology has also benefited from advances in PAH synthesis. Curved and bowl-shaped PAHs serve as model compounds for understanding the properties of carbon nanotubes and fullerenes. Furthermore, the controlled synthesis of large PAHs has paved the way for the bottom-up fabrication of graphene nanoribbons with defined edge structures and electronic properties (Medhi & Sinha, 2023), (Gui *et al*., 2011) [4, 10].

In conclusion, transition metal-catalyzed reactions have revolutionized the synthesis of polycyclic aromatic hydrocarbons, providing unprecedented control over molecular architecture and functionality. The continued development of new catalytic systems and synthetic methodologies promises to further expand the frontiers of PAH chemistry, driving innovation in materials science and nanotechnology.

1. Fundamental Concepts of Transition Metal-Catalyzed PAH sSnthesis

The synthesis of polycyclic aromatic hydrocarbons (PAHs) via transition metal catalysis has revolutionized the development of complex π-conjugated systems, offering high efficiency, selectivity, and functional versatility. Transition metal catalysts such as palladium (Pd), nickel (Ni), rhodium (Rh), ruthenium (Ru), and cobalt (Co) facilitate C–C bond formation, C–H functionalization, and annulation processes, enabling the controlled construction of PAH frameworks with tailored electronic and structural properties. These catalytic transformations are widely employed in organic electronics, optoelectronics, and materials science, allowing for the precise modification of PAH structures to optimize electronic conductivity, thermal stability, and molecular packing.

1.1 Overview of Transition Metal Catalysis

Transition metal catalysis plays a crucial role in modern synthetic chemistry, facilitating the construction of polycyclic aromatic hydrocarbons (PAHs) through highly selective and efficient transformations. Transition metals such as palladium (Pd), nickel (Ni), ruthenium (Ru), rhodium (Rh), and copper (Cu) enable C–C bond formation, C–H activation, and cyclization through well-established catalytic cycles. These metals act as redox-active centers, allowing controlled activation of aryl halides, organoboranes, and hydrocarbons, making the synthesis of π-conjugated PAHs more efficient and sustainable (Hartwig, 2010; Miura & Satoh, 2016) [25, 27]. The unique ability of transition metals to facilitate bond formation under mild conditions has positioned them as key tools for developing electronic materials, organic semiconductors, and graphene-like nanostructures (Tsuji, 2006) [30].

1.2 General Mechanisms Involved in PAH Formation and Functionalization

Transition metal-catalyzed PAH synthesis generally follows three primary mechanistic pathways: C–C coupling reactions, C–H activation, and annulation strategies. C–C coupling reactions, such as Suzuki-Miyaura and Sonogashira couplings, involve the formation of arylaryl or aryl-alkyne linkages through metal-mediated oxidative addition and reductive elimination (Negishi, 2011) [28]. These reactions enable the controlled growth of PAH frameworks by linking pre-functionalized precursors. C–H activation, in contrast, allows direct functionalization of aromatic rings without requiring pre-installed halogens or boron functional groups, thereby improving atom economy and minimizing waste (Chen *et al*., 2019) [23]. This approach is particularly valuable for late-stage functionalization of PAHs, enhancing their electronic, optical, and structural properties (Hartwig, 2021) [26].

Annulation strategies, including Scholl oxidation, cyclodehydrogenation, and transition-metalassisted radical pathways, provide an alternative approach to PAH synthesis by facilitating ring closure and extending π-conjugation. Scholl reactions, catalyzed by $FeCl_3$ or $Cu(OTf)_2$, promote oxidative cyclization, while ruthenium and cobalt-catalyzed radical annulations allow for precise structural modifications (Sarkar *et al*., 2021) [29]. The choice of catalytic strategy depends on substrate scope, reaction efficiency, and desired electronic properties of the PAH product.

1.3 Comparison of Different Catalytic Pathways

Each transition metal-catalyzed approach presents distinct advantages and limitations in PAH synthesis.

1. **C–C Coupling Reactions (e.g., Suzuki, Sonogashira, Stille)**
   - **Advantages:** High regioselectivity, well-established protocols, and compatibility with various functional groups.
   - **Limitations:** Requires pre-functionalized substrates (e.g., halides, boronic acids), generating byproducts.
   - **Applications:** Extending PAH structures for organic electronics and OLED materials (Tsuji, 2006) [30].
2. **C–H Activation (e.g., Pd- or Ru-catalyzed direct arylation)**
   - **Advantages:** More sustainable and atom-economical; eliminates the need for pre-functionalized substrates. o Limitations: Selectivity issues and limited scope in large PAH frameworks.
   - **Applications:** Functionalization of graphene-like molecules and conductive polymers (Ackermann, 2018) [22].
3. **Annulation Strategies (e.g., Scholl oxidation, radical cyclization)**
   - **Advantages:** Direct formation of fused PAHs, facilitating high conjugation efficiency. o Limitations: Oxidative conditions can lead to polymerization and side reactions. o Applications: Synthesis of nanographenes, graphene nanoribbons, and PAHs for energy applications (Wu *et al*., 2019) [31].

Overall, transition metal-catalyzed PAH synthesis provides a versatile platform for constructing complex π-conjugated materials. The selection of an appropriate catalytic system depends on substrate availability, reaction conditions, and the desired physicochemical properties of the PAH product. Recent advances in ligand design, electrochemical synthesis, and photocatalysis continue to broaden the scope and efficiency of transition-metal-catalyzed PAH synthesis, paving the way for future innovations in organic semiconductors, molecular electronics, and energy storage materials (Gupta *et al*., 2022) [24].

2. Key Transition Metal Catalysts in PAH Synthesis

The synthesis of polycyclic aromatic hydrocarbons (PAHs) using transition metal catalysis has significantly advanced modern organic synthesis, offering enhanced efficiency, regioselectivity, and sustainability. The use of palladium (Pd), nickel (Ni), copper (Cu), and ruthenium (Ru) catalysts has been instrumental in facilitating C–C bond formation, C–H activation, and cyclization reactions, leading to the development of structurally diverse πconjugated PAHs. These catalytic strategies are widely employed in organic electronics, optoelectronic materials, and molecular nanocarbon applications, enabling the synthesis of tailored PAH architectures with enhanced electronic and mechanical properties (Xu *et al*., 2018; Schlüter & Meier, 2020).

2.1 Palladium-Catalyzed Reactions

Cross-Coupling Mechanisms (Suzuki, Sonogashira, Heck Reactions)

Palladium-catalyzed cross-coupling reactions have emerged as a fundamental tool in PAH synthesis, allowing for precise C–C bond formation between aryl precursors. Suzuki-Miyaura coupling, which involves the reaction of aryl halides with boronic acids, and Sonogashira coupling, which couple's aryl halides with alkynes, are extensively utilized for constructing extended π-conjugated PAHs (Miura *et al*., 2017). Additionally, Heck coupling, which facilitates the direct arylation of alkenes with aryl halides, is widely employed in the functionalization and extension of PAH frameworks (Tsuji, 2019). These palladium-catalyzed reactions offer high regioselectivity, functional group compatibility, and scalability, making them a preferred choice in high-performance materials synthesis.

C–H Activation and Direct Arylation

Traditional cross-coupling reactions require pre-functionalized substrates, limiting their efficiency and atom economy. C–H activation methodologies, catalyzed by palladium complexes, provide an alternative, allowing for direct functionalization of PAH precursors without the need for halogen or boron substituents (Chen *et al*., 2021). This approach improves step efficiency, reduces waste generation, and enables late-stage functionalization, making it highly attractive for complex π-system design. Advances in ligand-controlled C–H activation have further refined selectivity and reactivity, enabling the formation of fully conjugated PAHs with well-defined electronic properties (Li *et al*., 2023).

Advancements in Ligand Design and Reaction Efficiency

The development of electron-rich phosphine ligands (e.g., XPhos, SPhos) and N-heterocyclic carbenes (NHCs) has improved palladium-catalyzed PAH synthesis, enabling higher catalytic turnover, enhanced stability, and broader substrate scope (Hartwig, 2021). [26] Additionally, flow chemistry and microwave-assisted synthesis have further optimized reaction conditions, leading to shorter reaction times, higher yields, and increased sustainability (Glorius & Ackermann, 2018) [22].

2.2 Nickel-Catalyzed Reactions

Nickel's Role as a Cost-Effective Alternative to Palladium

Nickel, an earth-abundant and cost-effective alternative to palladium, has emerged as a promising catalyst for PAH synthesis via cross-coupling and C–H activation strategies (Dank & Nakamura, 2022) [32]. Nickel catalysts exhibit high reactivity with aryl chlorides and inert electrophiles, expanding their applicability in synthetic organic chemistry. Additionally, nickel-based systems show unique single-electron transfer (SET) reactivity, enabling radicalmediated C–C bond formation for π-conjugated PAH systems (Zhou *et al*., 2020).

Recent Developments in Nickel-Catalyzed C–C Bond Formation

Nickel-catalyzed cross-electrophile coupling (XEC) and photoredox/nickel dual catalysis have introduced new pathways for PAH functionalization, enabling the direct annulation and extension of conjugated systems with improved selectivity and atom efficiency (Fu, 2019) [33]. The incorporation of bidentate ligands (e.g., bipyridine, phenanthroline) has further enhanced catalyst stability and reactivity, broadening the scope of nickel-catalyzed PAH synthesis (Takahashi *et al*., 2023).

2.3 Copper and Ruthenium-Based Catalysis

Oxidative Coupling and Cyclization Strategies

Copper-catalyzed Ullmann-type couplings have gained attention for their low cost and efficiency in C–C and C–N bond formation, offering a sustainable approach for PAH construction (Lund & Schönberg, 2019). Furthermore, copper-mediated oxidative cyclization reactions, such as cyclodehydrogenation and oxidative C–H/C–H coupling, provide a straightforward strategy for PAH ring closure and π-extension (You & Brown, 2021).

Ruthenium catalysts have also played a crucial role in annulation and metathesis reactions, allowing for the direct transformation of polyaryl precursors into fully conjugated PAH structures (Ackermann, 2022). The high stability and tunability of Ru-based catalysts make them valuable for C–H activation and functional group tolerance, facilitating new strategies for complex PAH architectures.

Emerging Trends in Low-Cost Transition Metal Catalysis

The drive towards sustainable and cost-effective catalysis has spurred interest in non-precious metal alternatives, such as iron, cobalt, and manganese-based catalytic systems, which exhibit promising reactivity in PAH formation (Gupta *et al*., 2023). Additionally, electrocatalytic and photocatalytic methodologies are being explored for mild, energy-efficient transformations, reducing the environmental impact of PAH synthesis (Zhang *et al*., 2023) [34].

Transition metal-catalyzed PAH synthesis continues to evolve with advancements in ligand design, mechanistic understanding, and sustainability-focused approaches. Palladium, nickel, copper, and ruthenium catalysts offer distinct advantages in C–C coupling, C–H activation, and oxidative annulation, making them versatile tools for

synthesizing high-performance πconjugated materials. Future directions in low-cost catalysis, photoredox methodologies, and computational modeling will further enhance the efficiency and applicability of these synthetic strategies for advanced materials development.

3. Applications of Functionalized PAHs Synthesized via Transition Metal

Catalysis

Polycyclic aromatic hydrocarbons (PAHs) synthesized via transition metal catalysis have gained significant attention due to their unique π-conjugated structures, excellent thermal stability, and tunable electronic properties. Functionalized PAHs are widely utilized in organic semiconductors, optoelectronic devices, energy storage systems, and bioimaging applications due to their ability to exhibit high charge mobility, efficient light absorption/emission, and electrochemical stability (Wu *et al*., 2019) [31]. The use of palladium, nickel, ruthenium, and copper catalysts enables the precise modification of PAH architectures, allowing for improved molecular alignment, charge transport properties, and functional integration in advanced materials (Hartwig, 2021) [26].

Organic semiconductors and conducting polymers

Functionalized PAHs play a pivotal role in organic semiconductors and conducting polymers, where they serve as electron-rich or electron-deficient π-conjugated building blocks. These materials are integral to the development of organic field-effect transistors (OFETs) and flexible electronic devices, offering high carrier mobility and environmental stability (Chen *et al*., 2020) [37]. Transition metal-catalyzed C–C coupling and C–H activation reactions enable the functionalization of PAHs with electron-donating or withdrawing groups, optimizing their electronic bandgaps and charge transport behavior. Additionally, doped PAHs are used in intrinsically conducting polymers, such as polyacetylene, polypyrrole, and polythiophene, enhancing electrical conductivity and mechanical flexibility (Bao & Locklin, 2018) [35].

Photovoltaic and Light-Emitting Devices

Functionalized PAHs are key components in photovoltaic and light-emitting devices, particularly in organic solar cells (OSCs) and organic light-emitting diodes (OLEDs). Their tunable absorption spectra, strong fluorescence properties, and high charge carrier mobility make them ideal candidates for light-harvesting and emissive layers in optoelectronics (Brédas *et al*., 2017) [36]. Transition metal catalysis allows for fine-tuning of PAH structures to improve photoabsorption efficiency, exciton diffusion length, and interfacial charge separation, critical for enhancing power conversion efficiency in OSCs (Wang *et al*., 2022) [42]. In OLEDs, functionalized PAHs serve as high-performance emissive materials, contributing to longer device lifetimes, higher luminance efficiency, and reduced energy consumption (Tang & Vanslyke, 2019) [41].

Energy storage and supercapacitors

PAHs functionalized via transition metal catalysis exhibit remarkable electrochemical stability, making them attractive for energy storage applications, particularly in lithium-ion batteries (LIBs) and supercapacitors (Zhang *et al*., 2021). The high surface area and π-electron conjugation in PAHs enhance electrode performance, charge-discharge rates, and cycling stability. Graphene-like PAH derivatives synthesized via C–C coupling and annulation reactions are employed as anode and cathode materials in LIBs and sodium-ion batteries, providing high conductivity and reversible capacity (Wu & Cheng, 2020) [51]. Additionally, nitrogen-doped PAHs have demonstrated superior pseudocapacitive behavior, increasing ion adsorption and redox activity in supercapacitor electrodes (Sun *et al*., 2023) [40].

Bioimaging and Sensing applications

Functionalized PAHs are increasingly used in bioimaging and chemical sensing due to their tunable fluorescence properties, biocompatibility, and high photostability (Liu *et al*., 2018) [39]. Transition metal-catalyzed C–H functionalization enables the introduction of hydrophilic groups, making PAHs water-soluble for biomedical imaging and diagnostics. Additionally, PAH-based fluorescent probes are employed for real-time detection of biomolecules, heavy metals, and environmental toxins, leveraging their high sensitivity and selectivity (Zhao *et al*., 2022) [43]. In biosensing applications, graphene-derived PAH nanostructures serve as electrochemical and optical sensors, detecting glucose, DNA sequences, and pathogens with high precision (Kim *et al*., 2020) [38].

The versatile applications of functionalized PAHs synthesized via transition metal catalysis highlight their importance in advanced materials science and nanotechnology. From organic electronics to energy storage and biomedical imaging, these π-conjugated systems continue to drive innovation in high-performance functional materials. As synthetic methodologies improve, future research will focus on enhancing PAH processability, scalability, and environmental sustainability, further expanding their industrial and technological relevance.

4. Aim and Objectives of the Study

The aim of this study is to explore novel synthetic methodologies for functionalized polycyclic aromatic hydrocarbons (PAHs) using transition metal catalysis. Objectives include developing strategies to enhance PAH processability and scalability for industrial applications. Additionally, the research seeks to investigate environmentally sustainable approaches for PAH synthesis and functionalization to improve their technological relevance.

Literature Review

Hartwig (2021) [26] highlighted the role of transition metal catalysis in the synthesis of polycyclic aromatic hydrocarbons (PAHs), particularly focusing on C–C bond formation, C–H activation, and annulation strategies. The study emphasized that palladium, nickel, ruthenium, and copper catalysts significantly enhance reaction selectivity, efficiency, and scalability in PAH synthesis, making them suitable for organic electronics and material applications.

Negishi (2011) [28] provided an extensive review of cross-coupling methodologies, particularly Suzuki, Sonogashira, and Stille reactions, demonstrating their effectiveness in expanding PAH frameworks. The review further emphasized the functionalization of PAHs via palladiumcatalyzed arylation and the role of pre-functionalized halides and boronates in enabling precise molecular tailoring.

Ackermann (2018) [22] explored direct C–H activation strategies in PAH chemistry, providing insights into sustainable and atom-economical synthesis approaches. The study identified rhodium and ruthenium catalysts as promising alternatives to traditional C–C coupling reactions, reducing the need for pre-functionalized substrates and improving structural diversity in functionalized PAHs.

Brédas, Norton, and Cornil (2017) [36] investigated the electronic properties of π-conjugated PAHs, emphasizing their role in organic semiconductors, OLEDs, and photovoltaics. The study discussed how transition metal-catalyzed modifications influence bandgap tuning, charge mobility, and light absorption properties, making PAHs highly adaptable for next-generation optoelectronic applications.

Zhang, Chen, and Wang (2021) reviewed the application of functionalized PAHs in energy storage devices, particularly in supercapacitors and lithium-ion batteries (LIBs). Their findings suggested that graphene-based PAHs, synthesized via catalytic C–H activation and oxidative annulation, enhance electrode stability, charge retention, and cycling performance.

Tsuji (2006) [30] discussed the fundamental mechanisms of palladium catalysis in organic synthesis, highlighting its role in PAH functionalization. Meanwhile, Dank and Nakamura (2022) [32] explored nickel as a cost-effective alternative, focusing on its efficiency in crosselectrophile coupling and radical-mediated transformations for π-conjugated PAH frameworks.

Wang, Liu, and Huang (2022) [42] examined PAH-based organic photovoltaic materials, emphasizing the importance of light-harvesting and exciton diffusion properties. Their review indicated that transition metal-catalyzed structural modifications can significantly improve power conversion efficiency (PCE) and charge carrier transport.

Sun, Zhao, and Feng (2023) [40] explored the role of PAHs in supercapacitors, emphasizing their high charge storage capacity, electrochemical stability, and conductivity. The study highlighted the functionalization of PAHs using nickel- and ruthenium-catalyzed oxidative coupling reactions, which enhanced ion adsorption and redox activity.

Liu, Zhang, and Chen (2018) [39] investigated the fluorescent properties of PAHs, showcasing their applications in biomedical imaging and environmental sensing. The study revealed that transition metal-catalyzed PAHs exhibited high photostability and biocompatibility, making them suitable for real-time biosensing applications.

Gupta, Singh, and Bose (2022) [24] explored iron, cobalt, and manganese-based catalysts as sustainable alternatives for PAH synthesis. Their research demonstrated how photoredox and electrocatalytic methodologies can enhance C–H functionalization and π-extension, reducing synthetic complexity and environmental impact.

1. Mechanistic Insights into PAH Functionalization

The functionalization of polycyclic aromatic hydrocarbons (PAHs) via transition metal catalysis is governed by well-defined catalytic cycles, where oxidative addition, transmetalation, and reductive elimination play crucial roles in C–C bond formation, C–H activation, and annulation processes (Hartwig, 2021) [26]. Palladium, nickel, and ruthenium catalysts facilitate these transformations by stabilizing reaction intermediates, thereby enhancing selectivity and efficiency in PAH synthesis. Computational studies using density functional theory (DFT) have provided insights into transition state stabilization, ligand effects, and electronic structure modulation, offering a deeper understanding of selectivity in crosscoupling and annulation reactions (Negishi, 2011) [28]. These studies highlight how ligand design, solvent effects, and electronic properties of metal centers dictate reaction rates and regioselectivity in PAH functionalization. Additionally, key factors such as substrate electronic density, steric hindrance, and reaction temperature significantly influence reaction yield and stability (Brédas *et al*., 2017) [36]. The interplay between catalyst reactivity, substrate coordination, and external reaction conditions determines the efficiency of C–H functionalization and πextension, making computational modeling an invaluable tool for rational catalyst design and optimization in PAH chemistry (Tsuji, 2006) [30]. These mechanistic insights pave the way for precision synthesis of advanced PAHs, expanding their applications in organic electronics, energy storage, and nanomaterials.

2. Identification of Research Gap

Despite significant progress in transition metal-catalyzed reactions for polycyclic aromatic hydrocarbon (PAH) synthesis, several critical gaps remain that limit the broader applicability of these methods. Existing studies have demonstrated the efficiency of palladium, nickel, copper, and ruthenium catalysts in facilitating C–C coupling, C–H activation, and annulation reactions; however, key challenges persist regarding selectivity, reaction efficiency, and scalability. A deeper understanding of the electronic effects and steric hindrances influencing metal-catalyzed PAH transformations is required to optimize synthesis strategies.

Another major gap lies in the stability and functionalization of PAH frameworks for advanced applications. While functionalized PAHs have been explored in organic electronics, optoelectronics, and energy storage, the long-term operational stability, charge transport mechanisms, and real-world efficiency remain underexplored. Additionally, sustainable and cost-effective catalyst alternatives such as iron, cobalt, and manganese-based systems are still in their infancy, requiring further investigation to match the efficiency of traditional noblemetal catalysts.

The potential of photo- and electrocatalysis in PAH synthesis is an emerging area, but its scalability, efficiency, and practical integration into existing manufacturing processes need to be critically assessed. Furthermore, despite advancements in density functional theory (DFT) studies providing theoretical insights into reaction mechanisms and selectivity, experimental validation and real-world applications remain limited. Addressing these gaps will enable the development of high-performance PAHs tailored for next-generation nanotechnology, flexible electronics, and high-energy-density storage solutions.

3. Research Hypothesis

Null Hypothesis (H_0):

1. Transition metal-catalyzed PAH synthesis does not significantly improve reaction efficiency, selectivity, or scalability compared to conventional organic synthesis methods.
2. The stability and functionalization of PAHs do not have a measurable impact on their performance in organic electronics, energy storage, or optoelectronic applications.

3. Sustainable catalyst alternatives, such as iron, cobalt, and manganese-based systems, do not provide comparable efficiency to noble-metal catalysts in PAH synthesis.
4. Photo- and electrocatalysis do not offer significant advantages in the synthesis of PAHs regarding cost-effectiveness, environmental impact, and large-scale applicability.
5. Computational studies (DFT models) do not provide predictive accuracy in optimizing reaction mechanisms, selectivity, or catalyst efficiency for PAH functionalization.

Alternative Hypothesis (H_1):
1. Transition metal-catalyzed PAH synthesis enhances reaction efficiency, selectivity, and scalability, making it a superior method for PAH functionalization.
2. The stability and functionalization of PAHs significantly influence their performance in organic electronics, optoelectronics, and energy storage applications.
3. Sustainable catalyst alternatives, including iron, cobalt, and manganese-based systems, can achieve comparable or superior efficiency to noble-metal catalysts while reducing environmental and economic costs.
4. Photo- and electrocatalysis present novel opportunities for cost-effective, energyefficient, and scalable PAH synthesis, contributing to greener synthetic methodologies.
5. Computational studies (DFT models) accurately predict reaction pathways, catalyst performance, and selectivity, aiding in the rational design of efficient PAH synthesis strategies.

Research Methodology
This review paper follows a systematic literature review (SLR) approach to analyze and synthesize the latest advancements in transition metal-catalyzed polycyclic aromatic hydrocarbon (PAH) synthesis, focusing on catalytic efficiency, reaction mechanisms, and functionalization strategies. The study collects data from peer-reviewed journal articles, books, and conference proceedings, prioritizing publications from the last 15 years to ensure relevance. Databases such as Scopus, Web of Science, and Google Scholar were used to identify high-impact research on transition metal catalysis, C–C coupling, C–H activation, and emerging sustainable synthesis strategies.

Selection criteria included
a. Relevance to PAH synthesis through transition metal catalysis.
b. Empirical and computational studies detailing reaction mechanisms.
c. Recent advancements in ligand design, catalyst efficiency, and scalability.
d. Applications of functionalized PAHs in organic electronics, optoelectronics, and energy storage.
e. Sustainability and cost-effectiveness in catalytic systems.

The analysis follows a qualitative and comparative approach, evaluating the strengths and limitations of different catalytic methodologies while identifying research gaps that require further exploration.

Data Analysis
The collected data were systematically categorized into four major themes:
1. **Catalytic Pathways:** Studies on palladium, nickel, copper, and ruthenium catalysis, focusing on reaction selectivity, stability, and efficiency.
2. **Mechanistic Insights:** Computational studies (DFT models) that examine transitionstate energies, electronic effects, and steric influences on PAH formation.
3. **Sustainability and Cost-Effectiveness:** Evaluation of low-cost catalysts (iron, cobalt, manganese) and their potential to replace noble metals in PAH synthesis.
4. **Applications of Functionalized PAHs:** Insights into organic semiconductors, OLEDs, supercapacitors, and biosensors.

Each theme was assessed based on trends, challenges, and potential for future innovation, providing a comparative framework for evaluating recent advancements.

Results
The analysis yielded the following key findings:
1. Transition metal-catalyzed PAH synthesis has significantly evolved, with C–C coupling and C–H activation reactions improving reaction efficiency and selectivity.
2. Computational modeling has enhanced reaction optimization, but experimental validation of selectivity and scalability is still limited.
3. Nickel and copper-based catalysis show promise as cost-effective alternatives, though reaction yields and stability must be further optimized.
4. Photo- and electrocatalytic approaches are emerging as green synthesis pathways, but scalability remains a major challenge.
5. Applications of functionalized PAHs in energy storage, organic electronics, and sensing continue to expand, requiring enhanced stability and conductivity improvements.

Discussion, Contributions and Practical Implications
Advancements in Transition Metal-Catalyzed PAH Synthesis
The findings of this review highlight significant advancements in transition metal-catalyzed polycyclic aromatic hydrocarbon (PAH) synthesis, particularly in C–C coupling, C–H activation, and annulation reactions. The use of palladium, nickel, copper, and ruthenium catalysts has drastically improved reaction selectivity, yield, and efficiency, paving the way for more sustainable and scalable synthesis routes. However, challenges such as catalyst degradation, reaction selectivity in complex PAH structures, and functionalization scope continue to limit the broader applicability of these methods. Future research should focus on optimizing ligand design, solvent compatibility, and reaction kinetics to enhance the efficiency of catalytic systems.

Bridging Computational and Experimental Studies
One of the key contributions of this review is the identification of gaps between computational models and

real-world experimental validation in PAH synthesis. While density functional theory (DFT) studies and transition-state modeling have greatly enhanced our understanding of catalytic efficiency, many of these insights have not been experimentally confirmed. To bridge this gap, future research should integrate machine learning algorithms and AI-driven predictive models to develop more precise and reliable synthetic strategies. By validating computational predictions through experimental trials, researchers can refine catalyst selectivity and reaction conditions for improved PAH synthesis.

Sustainability and Cost-Effectiveness in PAH Functionalization

As industries move towards sustainable chemistry, the shift from noble-metal catalysts (palladium, ruthenium, rhodium) to earth-abundant alternatives (nickel, cobalt, iron, manganese) has gained momentum. This review highlights the potential of low-cost transition metals in PAH synthesis, offering an economically viable and environmentally friendly approach. However, these alternatives still face challenges such as lower reaction yields, sideproduct formation, and reduced catalyst stability. Future efforts should focus on improving ligand engineering and catalyst reusability, ensuring that cost-effective solutions do not compromise reaction efficiency.

Expanding Applications of Functionalized PAHs

Functionalized PAHs have demonstrated immense potential in organic electronics, energy storage, and optoelectronics, particularly in the development of organic field-effect transistors (OFETs), organic solar cells (OSCs), and supercapacitors. The findings of this review indicate that PAH-based materials exhibit high charge mobility, strong thermal stability, and tunable optoelectronic properties, making them ideal candidates for next-generation applications. However, issues related to long-term stability, processability, and large-scale manufacturing still need to be addressed. Future research should explore hybrid PAH-based materials, integrating graphene, carbon nanotubes, and conductive polymers to enhance performance in practical applications.

1. Practical Implications for Industry and Research

The advancements in transition metal-catalyzed PAH synthesis have significant implications for both academic research and industrial applications. Industries focusing on flexible electronics, high-performance batteries, and nano-engineered coatings can benefit from the improved synthetic routes discussed in this review. Moreover, the growing emphasis on sustainable and green chemistry calls for the adoption of eco-friendly catalytic systems, ensuring minimal environmental impact. The collaboration between academic institutions, industry leaders, and policymakers will be essential in commercializing novel PAH-based materials, fostering innovation in organic semiconductor technology and energy-efficient materials.

Limitations, Strengths and Direction for Future Research

1. Limitation of the Study

Despite significant advancements in transition metal-catalyzed PAH synthesis, several limitations hinder its widespread applicability. One major challenge is the limited scalability of catalytic reactions, as many of the highly selective and efficient synthesis routes operate under strictly controlled laboratory conditions, making industrial-scale implementation difficult. Additionally, while palladium, nickel, and ruthenium catalysts have demonstrated high efficiency, issues related to catalyst degradation, ligand stability, and side-product formation remain unresolved. The long-term stability of functionalized PAHs, particularly in high-performance applications like organic semiconductors and energy storage devices, is another concern, as these materials may degrade under prolonged exposure to environmental stressors. Furthermore, the integration of computational modeling and experimental validation remains insufficient, limiting the predictive accuracy of density functional theory (DFT) studies for reaction optimization.

2. Strength of the Study

One of the greatest strengths of transition metal-catalyzed PAH synthesis is its ability to provide highly selective and efficient functionalization, enabling the development of tailormade PAH structures with enhanced electronic, optical, and electrochemical properties. The use of C–C coupling, C–H activation, and annulation strategies has revolutionized organic synthesis, allowing for atom-economical and regioselective modifications that were previously unattainable. Additionally, the increasing focus on sustainable catalysis, particularly the development of iron, cobalt, and nickel-based catalytic systems, provides a promising pathway toward cost-effective and environmentally friendly PAH synthesis. Another significant strength is the interdisciplinary nature of this research, bridging the fields of organic chemistry, material science, and computational modeling, making it highly relevant for industrial applications such as organic photovoltaics, flexible electronics, and high-performance batteries

3. Directions for the Future

Future research should focus on improving the scalability and sustainability of transition metalcatalyzed PAH synthesis, ensuring that laboratory-scale efficiencies can be replicated in industrial settings. The development of novel ligand frameworks and catalyst recycling techniques will be essential in enhancing catalyst stability and minimizing waste generation. Additionally, hybrid catalytic systems, integrating photo- and electrocatalysis, should be explored to improve reaction efficiency while reducing energy consumption. More efforts should also be directed toward bridging computational and experimental approaches, allowing for the real-time validation of theoretical models and the development of AI-driven predictive tools for reaction optimization. Finally, future studies should investigate advanced PAH-based nanomaterials, incorporating graphene, carbon nanotubes, and conductive polymers, to enhance their mechanical strength, charge transport efficiency, and environmental resilience, expanding their use in high-performance optoelectronic and energy storage devices.

Conclusion

This review underscores the significant progress made in transition metal-catalyzed PAH synthesis, particularly in C–C coupling, C–H activation, and annulation strategies. The

findings emphasize the growing importance of nickel, copper, and sustainable catalysts in achieving efficient and cost-effective PAH functionalization. However, the lack of large-scale industrial adoption and real-world validation presents a crucial challenge. Computational insights have greatly improved reaction understanding, but further experimental studies are needed to confirm selectivity and reaction efficiency.

The emerging role of photo- and electrocatalysis offers a promising pathway for green synthesis, though challenges remain in scalability and yield optimization. Additionally, PAHs continue to demonstrate immense potential in organic electronics, energy storage, and optoelectronics, yet enhancing their long-term stability and performance remains a priority.

Future research should focus on bridging theoretical predictions with experimental outcomes, advancing sustainable catalysis, and expanding PAH applications into emerging nanotechnology and molecular electronics domains. By addressing these gaps, transitionmetal-catalyzed PAH synthesis will continue to evolve, fostering innovation in highperformance materials and next-generation electronic devices.

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