



Non-traditional Ligands in Coordination Chemistry: A Review of Small Molecules Activation and Catalysis

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Received: 14th Jan 2026; Revised: 25th Jan 2026; Accepted: 05th Feb 2026

Abstract: Traditional ligands well proven in the field of coordination chemistry include amines, phosphines and carboxylates. Nevertheless, recent years are characterized by a revolutionary change in the field of non-traditional ligands such as carbenes, nitrenes, borylenes, and ambiphilic species possessing novel electronic and steric properties and are challenging traditional paradigms in the field of coordination chemistry. In this review, we discuss the emerging frontier of these unconventional ligands, within the settings of small molecule activation, as well as homogeneous catalysis. Non-traditional ligands open up the boundary of catalysis by allowing mild conditions to activate inert molecules including H₂, N₂, CO₂, and CH₄ in a wide variety of bond breaking/making reactions. It focuses on the design of ligands, metal-ligand cooperativity and how these ligands mechanistically promote multi-electron transformations. The combination of spectroscopic, computational and structural data also illuminate the effect such new ligand frameworks have on reactivity, selectivity and stability. The review shows the recent breakthroughs and upcoming scope of exploiting non-conventional ligands in sustainable catalysis with particular focus on sustainable chemical transformations, energy conversion and fine chemical synthesis.

Keywords: Non-traditional Ligands, Small Molecule Activation, Catalysis, Metal-Ligand Cooperativity, Carbenes and Borylenes

How to cite this article: Abubakar MY, Anidobu CO, Kpesibe JF, Filibus D, Abdullahi KN, Apaji AN. Non-traditional ligands in coordination chemistry: A review of small molecules activation and catalysis. *NextGen Chem Discov.* 2026 Jan-Mar;2(1):34-43.

Conflict of interest: None

Introduction

Traditionally dominated by classical ligands including amines, phosphines, and carboxylates, coordination chemistry has over the past several years been completely changed by the advent of non-traditional ligand systems that have altered the accepted donor-acceptor paradigm. Such new ligand classes have been N-heterocyclic carbenes (NHCs), nitrenes, borylenes, and ambiphilic frameworks, which differ by having unusual steric and electronic behaviours, which allows metal complexes to achieve new levels of reactivity and coordination environments not previously accessible (1; 2).

Many non-traditional ligands are non-innocent (unlike classical ligands that most often play a spectator role in catalytic reactions), and they can be directly involved in bond activation, as well as redox reactions, by taking part in metal-ligand cooperativity (3). Examples include carbenes and borylenes, which may serve as both powerful 1-electron donors and 2-electron acceptors, and in other instances become the redox-active units mediating multi-electron reactions that are the foci of catalytic cycles (4). The potential of such dual reactivity has been key in the development of activation of kinetically and thermodynamically inert molecules like N_2 , CO_2 , CH_4 and H_2 that were conventionally not easily activated in mild conditions (5).

This new consideration of the small-molecule activation is motivated by global needs such as the establishment of sustainable energy systems, decarbonization, and environment friendly chemical reactions. Recent reports emphasize the potential of custom scaffolds of ligands to be selective and efficient to perform the transformation of small molecules without having to resort to harsh reaction conditions (6; 7). Redox-flexible or ambiphilic organic pincer-type ligands, e.g., have shown exceptional performance in the hybrid reversible hydrogenation and CO_2 reduction reactions and even in dehydrogenation catalysis (8; 9).

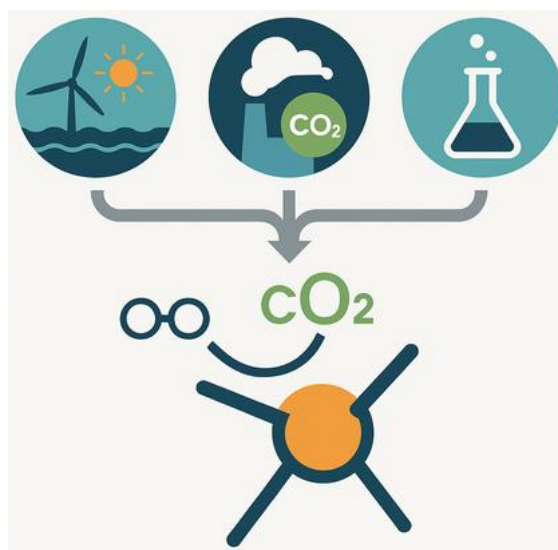


Figure 1: Integrating Renewable Energy, Carbon Capture, and Catalysis for CO_2 Utilization

Advances in Non-Traditional Ligand Design and Characterization

Advances in recent computational chemistry, high-resolution spectroscopy and time-resolved crystallography (e.g. X-ray), have particularly speeded up the rational design and mechanism knowledge of non-traditional systems of ligand in coordination chemistry. The dissimilarity in ligand parameter mapping—including those of electronic distribution, variability in bite angles, and steric profiles, and their effect on catalytic selectivity, stability, and rate—has now been possible with the help of these cutting-edge

tools to be performed in detail (10). Favorable quantum chemical techniques, such as the density functional theory (DFT) and ab initio molecular dynamics (AIMD) enabled forecasting and verification of metal ligand cooperativity trajectories and reactive intermediate (11; 12).

As an example, real-time changes in catalytic cycles with ambiphilic and redox-active ligands have been observed in spectroscopies that are active today, such as Mossbauer, EPR, and operando IR/Raman spectroscopy (13). On the same note, single-crystal X-ray diffraction (SCXRD) with synchrotron radiation has helped gain atomistic understanding on elusive intermediate states, further elucidating the cooperative ligand behaviour in bond activation processes (14). All these advances contribute to the establishment of ligand frameworks optimized to provide metal-ligand reactivity key to green and sustainable catalysis, such as CO₂ fixing, C-H bond-bond addition, and H₂ production (15).

This study goes in depth on the progress, structural variety and mechanistic functions of non-conventional ligand in coordination chemistry. Their applications are given particular emphasis when used in catalysing small molecules and in the homogeneous catalysis. It reviews new approaches to ligand design (such as ambiphilic, non-innocent, and cooperative frameworks), and their role in increased reactivity in mild and sustainable conditions. With this, the review also describes how non-traditional ligands contribute to the essential transformations of hydrogenation, selective C-H activation, and CO₂ activation as they directly interact with the catalytic processes through proton / electron transfer and the dynamic nature of the bonds.

Traditional vs. Non-Traditional Ligands: A Contemporary Perspective

Ligands continue to be the focus of the reactivity of metal complexes in contemporary coordination chemistry. Generally, distributed ligands (phosphines, amines, halides, and carbonyls) have been popular owing to their predictable bonding behavior, well-understood behavior of a σ -donor and a π -acceptor, as well as easy to understand structure. Such classical ligands bind metal centers in a variety of oxidation states and geometries and are central to a variety of core reactions such as hydroformylation, hydrogenation, and cross-coupling (16).

Nevertheless, in recent years unconventional ligands have proven to be highly useful alternatives, with their ability to be flexible and occasionally redox-active in terms of bonding. Examples of this new category are N-heterocyclic carbenes (NHCs), borylenes, nitrenes, and frustrated Lewis pairs (FLPs) that in many situations can be a dynamic part of the catalyst both in nucleophilic and base-metal-catalysis applications (17). They are involved in direct bond activation unrivalled by conventional ligands and this includes reversible proton or electron transfer, multiple bonding of metals and ligands, as well as synergistic interaction with substrate.

Non-conventional systems in a metal-ligand cooperative fashion afford a ligand to rein in catalytic roles shared with the metal center. As an illustration, it is possible to note the excellent efficiency of cooperative pincer ligands in reactions such as the hydrogenation of CO₂, reduction of N₂, and oxidative addition using ambient conditions (18). These systems are also commonly characterized by numerous reactive positions on which substrate binding and conversion can occur, in turn boosting per frequency and selectivity of conversion (19).

Furthermore, ligand-based reactivity opens new frontiers into the field of catalysis in which the ligand does not only affect but also acts to drive reaction pathways. The reaction is essential in allowing the atom-economical, low energy routes towards green chemistry compliance. Due to this, non-conventional ligands have risen to be an invaluable assistant in the rational creation of the next generation of catalysts that address the increasing requirements of efficient and sustainable chemical procedures.

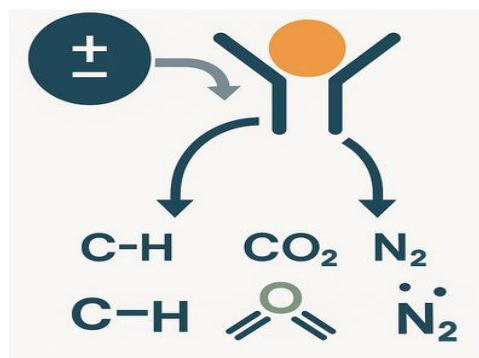


Figure 2: Metal-Ligand Cooperative Catalysis for Small Molecule Activation: C-H, CO₂, and N₂ Transformations

Advances in the synthesis of non-conventional ligand structures have led to an explosive increase in the scope of uses of the coordination complexes in the activation of small molecules. Among the key strengths of such ligands are the structural and electronic versatility that allows these ligands to tightly control catalytic activity. Modern ambiphilic ligands have flexible environments of bonding unlike their inflexible traditional analogues and may be able to adapt to electrochemical variations at the central metal atom or attachment of incoming substrates thereby affording greater control over reactivity and selectivity and sustainability (20; 21).

Developments have also focused on synergies between geo-normal metals and the non-traditional ligands in the recent past. Such bonding combinations have the ability to produce unconventional oxidation states of such familiar base metals as Fe, Co, and Mn, and catalyze transformations that were believed to only be available to noble metals (22). It is especially important that such a shift is made in the course of seeking green chemistry as it makes possible the use of catalytic processes and procedures which are also economically and environmentally sustainable. Consequently, it has resulted in the essentiality of non-traditional ligands when designing future catalysts in the fine chemical synthesis process, renewable energy conversion, and carbon management technology (23). Unlike their classical analogues, non-traditional ligands are multifunctional, with potential redox activity, and have proton/electron transfer and cooperative bonding modes of action. The properties assist in the maintenance of Metal Ligand Cooperativity (MLC) in which the metal center, and the ligand itself, have direct participation in the conversion of the substrate, which lessens the energy costs and enhances the efficiency of the turnover. Their use has re-established the horizons of coordination chemistry, where these ligands join the frontier of C-H activation, hydrogenation, CO₂ utilization and nitrogen fixation technologies.

Unique Properties of Non-Traditional Ligands

The development of non-conventional ligands in the 21st century can be described as intertwined with the evolution of the coordination chemistry as the novel class of ligands not only dismantles the traditionally accepted paradigms of metal-ligand bonding, but also provides novel experimental modes of reactivity. In contrast to classical ligands, which are normally associated with a one-dimensional role with static donation sigma-donation, and back-donation 4-donation, non-traditional ligands lead to ambiphilicity, non-innocence, and multi-site reactivity, which greatly expands catalytic potential (24; 25).

Borylenes and N-heterocyclic carbenes (NHCs) are examples of ambiphilic ligands that can be both an electron donor and an acceptor, stabilize metal centers in a wider range of oxidation states and enable *In Situ* electronic tuning. So, multi-step reactions and adaptive catalysis can be performed under different

conditions (26). Such properties play a critical role, especially, in the low-energy activation of bonds and multielectron reactions.

Other features of non-traditional ligands are the non-innocent behavior. Instead of being inert scaffolds these ligands are bonded directly to the process of redox, proton or even atom transfer process as a whole part of the catalytic mechanism. Another important example of such systems is those set up around the redox-active pincer ligands and the aromatization-dearomatization cycle, where the ligands reorganize in terms of structure or charge upon each turnover and allow hydrogenation, dehydrogenation, and C-H functionalization reactions to be realized at room-temperature (27).

Also, non-traditional ligands favor metal-ligand cooperativity (MLC), especially in heterolytic bonds breaking, e.g., the cleavage of H₂. The ligand/metal work in concert, with one somewhere accepting a proton, the other an hydride, to do the activation without either requiring high energy input (28). This provides a more durable, more efficient catalytic cycle having a broader scope in functional groups tolerance.

Such a central role is played by structural modularity as well. We can model or make ligands structures with bulky ligands, electron withdrawing groups or modular coordination sites that allow us to control carefully the substrate access or reaction pathways and transition state stabilization. This customization empowers chemists to fine-tune catalytic systems for specific applications, from selective C-H activation to CO₂ valorization (29).

Moreover, many non-traditional ligands exhibit multi-site reactivity, facilitating bimetallic or multinuclear complex formation, which in turn supports delocalized redox processes. These cooperative assemblies are especially valuable in N₂ activation and CO₂ electroreduction, where multiple electrons and protons must be transferred sequentially (30).

The ambiphilicity, redox activity, structural flexibility, and cooperative mechanisms intrinsic to non-traditional ligands position them as powerful tools in advancing sustainable catalysis and molecular-level reactivity control.

Applications in Small Molecule Activation and Catalysis

One of the most notable issues in the field is the complete activation of thermodynamically stable molecules at mild conditions, i.e., H₂, N₂, CO₂ and CH₄. It is the role of non-traditional ligands that, via metal ligand cooperativity and non-innocent behaviour, now take centre stage in overcoming this challenge (31).

Platinum-group metals once known to engage Hydrogen activation are now within reach with iron, cobalt or manganese complexes that use bifunctional ligands. Such systems have led to the heterolytic splitting of H₂, with the ligand accepting a proton and the metal accepting a hydride, with the activation energy being reduced greatly and functional group tolerance greatly increased (32).

Activation of nitrogen Another way is by using non-traditional ligands in low-valent metal complexes, which permit stepwise reduction through a 4p-backdonation into antibonding orbitals on N₂ to form a transition state complex. At the same time, redox-active ligands can act as a buffer to the electron transfer allowing controlled proton-coupled electron transfer (PCET) reactions. Such contributions provide an idea of how to perform artificial nitrogen fixation paths with the performance of nature nitrogenase enzymes (33).

In the same manner, the non-traditional ligands increase the CO₂ activation and reduction significantly through offering cooperative sites in nucleophilic attack and electron build-up. It has led to an innovation in the CO₂ -formate and CO₂ -methanol transformation via the base metals, which may become an opportunity of capturing and reusing carbon (CCU) (34).

Table 1: Activation of Small Molecules by Non-Traditional Ligands

Molecule	Challenge in Activation	Role of Non-Traditional Ligands	Key Strategies Enabled	Example Metals	References
H ₂	High bond dissociation energy; requires noble metals traditionally	Promote heterolytic cleavage through bifunctional (ambiphilic) ligand behavior	Metal accepts H ⁻ , ligand accepts H ⁺ ; lowers activation energy	Fe, Co, Mn	40
N ₂	Extremely stable triple bond (N≡N); poor nucleophile	Stabilize low-valent metals and support multi-electron redox chemistry	Back-donation to π^* orbitals; facilitate stepwise reduction and protonation	Mo, Fe, Ti	41
CO ₂	Thermodynamic and kinetic stability; linear geometry limits reactivity	Enable nucleophilic attack or reduction via metal-ligand synergy	Ligands assist in C=O bond polarization or multi-electron reduction pathways	Ru, Re, Ni	42
CH ₄	Strong C-H bond, high bond dissociation energy	Direct C-H activation via ligand-assisted proton/electron shuttling	Ligands offer proton or hydride acceptor sites to cleave C-H bonds	Ir, Rh, Cu	43

CO₂ Activation via Ligand-Metal Push-Pull Synergy

Converting stable green house gas such as CO₂ has emerged as a key in the sustainable chemistry. Contemporary ligand systems, in particular systems that actively polarize and activate CO₂, include internal Lewis acidic/basic sites (often in bimetallic architectures or in FLPHT or FLPHT strickly quota-squared system type systems). The complexation with a nucleophilic center at the metal and an electrophilic site (e.g. borane or zinc Lewis acid) within the ligand backbone, gives access to insertion of CO₂ into M-H, M-O, or M-N bonds to generate metal-carbon adducts. They can, instead, be turned into value added products (e.g., formate, methanol or carbonates) through mild processes (Corona *et al.*, 2022; PerezJimenez *et al.*, 2023).

Here, it is worth noting that the steric and electronic tuning of the metal and Lewis acidic partner greatly influences selectivity of the reaction, i.e. whether the CO₂ is trapped, cleaved or generates divergent reduced products, hence the significance of logical ligand design (35).

Methane Activation through Ligand-Enabled High-Valent Intermediates

The low energy of activation of the C-H bonds that are present in methane poses an enormous obstacle on their activation due to its high chemical stability. Recent computational work shows that ligating environments that can stabilize high-valent metaloxo or metalnitrado intermediates, particularly redox-active pincer ligands, have activation barriers to methane via the 0, 5, 5(6, 11) and oxidative hydrogen

migration pathways to be as low as ~ 17 kcal/mol (36). In comparison, other ligand systems, namely redox-noninnocent pincer complexes in the transition metals iron or cobalt, not only tune the energetics of a reaction, but can also be used selectively to functionalize the product (37).

Multistep Catalytic Cycles Enabled by Ligand Cooperation

Beyond CO₂ or CH₄, non-traditional ligands contribute critically to multistep catalytic cycles such as hydro functionalization, hydrogenation, and cross-coupling. By engaging in hydrogen bonding, proton relays, or reversible redox changes, these ligands stabilize reactive intermediates and transition states, often via Metal-Ligand Cooperativity (MLC). The result is a flexible, modular catalytic system with broad substrate scope and high turnover.

Catalytic Pathway Innovation via Non-Traditional Ligands

New ligand systems, e.g., NHCs, borylenes and multidonor-multif-acile donors (e.g., ambiphilic donors; FLP-type systems) have revolutionized catalysis by enabling reactions that could not be or would not be attempted. These ligands allow exploitation of new catalytic pathways, by stabilizing non-classical oxidation states, facilitating multielectron processes, and tuning metal electronics. Examples of such applications are transition-metal-boron FLP complexes that activate the CO₂ through push-pull donor-acceptor synergy, alter the bonding nature of CO₂, and as a result, trigger divergent transformations depending on the Lewis-acidic identity of the co-catalyst (38).

Unlike traditional spectator ligands, new ambiphilic systems have been found to successfully incorporate donating and accepting properties to provide catalytic efficiency in the cleavage of C-H or N₂ D bonds using the back-donation and FLP-like motive. Another recent development in catalytic chemistry involves non-traditional ligands also used to obtain irreversible or radical-based cleavage pathways that occur through ligand-centered redox cycling; e.g., pincer ligands containing redox-active homo-, hetero-, and peri-bonding (or bifunctional activation) can activate O₂ and related gases under milder conditions, and thus both efficiency and energy economy of catalytic cycles are enhanced.

In addition, ligand design has produced pathway bifurcation i.e. the ability of a single catalytic environment to react differently, according to different conditions, to yield different mechanisms or products through structural versatility in both steric and electronic terms. Examples of this are hydroamination and hydroboration systems, and hydrogenation where selectivity could be varied using external stimuli but the metal and ligand scaffold could remain unchanged.

Ligand Design and Metal-Ligand Cooperativity Focus

The current approach within the ligand design field is the direct incorporation of the chemical functionality, namely proton donor, proton acceptor, redox-active functionality, or the sites of coordination, into the backbone of ligand. Such association allows the Metal-Ligand Cooperativity (MLC) such that the ligand and metal are synergistic in the processes of bond-activation instead of complete independence. This strategy can be illustrated especially well by Pincer-type scaffolds such as PNP and PNN. These systems have the ability to heterolytically open H₂, add CO₂, and in a reversible fashion, product-shuffle protons, but in a synthetic system (35; 39). Rigid bite angles together with side-arms possessing Lewis acidic or basic characters has also allowed the frustrated Lewis pair (FLP) -like behaviour in metal complexes to be achieved, broadening the binding modes in terms of cooperative activation from conventional pincer systems (38).

Chemical Equations Illustrating Metal-Ligand Cooperativity (MLC)

- i. Electrolytic Cleavage of H₂ via Metal-Ligand Cooperativity (PNP Pincer System)
$$[M-NHR] + H_2 \rightarrow [M-H] + [NHR-H]^+$$
- ii. CO₂ Insertion into a Metal-Hydride Bond Assisted by a Cooperative Ligand
- iii. Nitrogen Activation by Low-Valent Metal-Ligand Complex
$$[M-L] + N_2 \rightarrow [M(N_2)-L] \rightarrow (e^-/H^+ \text{ stepwise}) \rightarrow NH_3$$
- iv. Ligand-Centered Radical Participation in Substrate Transformation
$$[M-L] + R-X \rightarrow [M-L\bullet-R] + X^-$$
- v. Frustrated Lewis Pair (FLP)-Like Reactivity with NHC-Boron Ligands
$$L-B + H_2 \rightarrow L-H^+ + B-H^-$$

Furthermore, ligand-centered reactivity is now being extended to sustainable catalysis, especially in base-metal systems (Fe, Mn, Co). By designing ligands that can compensate for the redox or electronic limitations of these cheaper metals, chemists have developed systems capable of mimicking noble-metal reactivity in hydrogenation, cross-coupling, and oxidation reactions.

Ultimately, the future of catalysis depends not only on identifying reactive metal centers but also on developing intelligently designed ligands that can act as molecular machines engaging, transforming, and releasing substrates in a controlled and cooperative manner.

Conclusion

Developing workable Metal-Ligand Cooperativity (MLC) catalysts has emerged as a salient theme concerning current catalytic research, but a few research areas remain to be filled. Despite the promise of non-traditional ligand structures (redox-active frames or ambiphilic frames) investigation has not gone much further, particularly within the context of pincer-type systems. The full potential of cooperative ligand design has not been exploited, nor have the possibilities of its being used to catalyze inactive substrates, such as nitrogen and methane. Further research should thus extend ligand scope, deeper mechanistic understanding and make a priority of using greener metals. MLC can change the way catalysts are used by performing fast, highly selective and environmentally friendly chemical conversions via systematic rational ligand design.

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