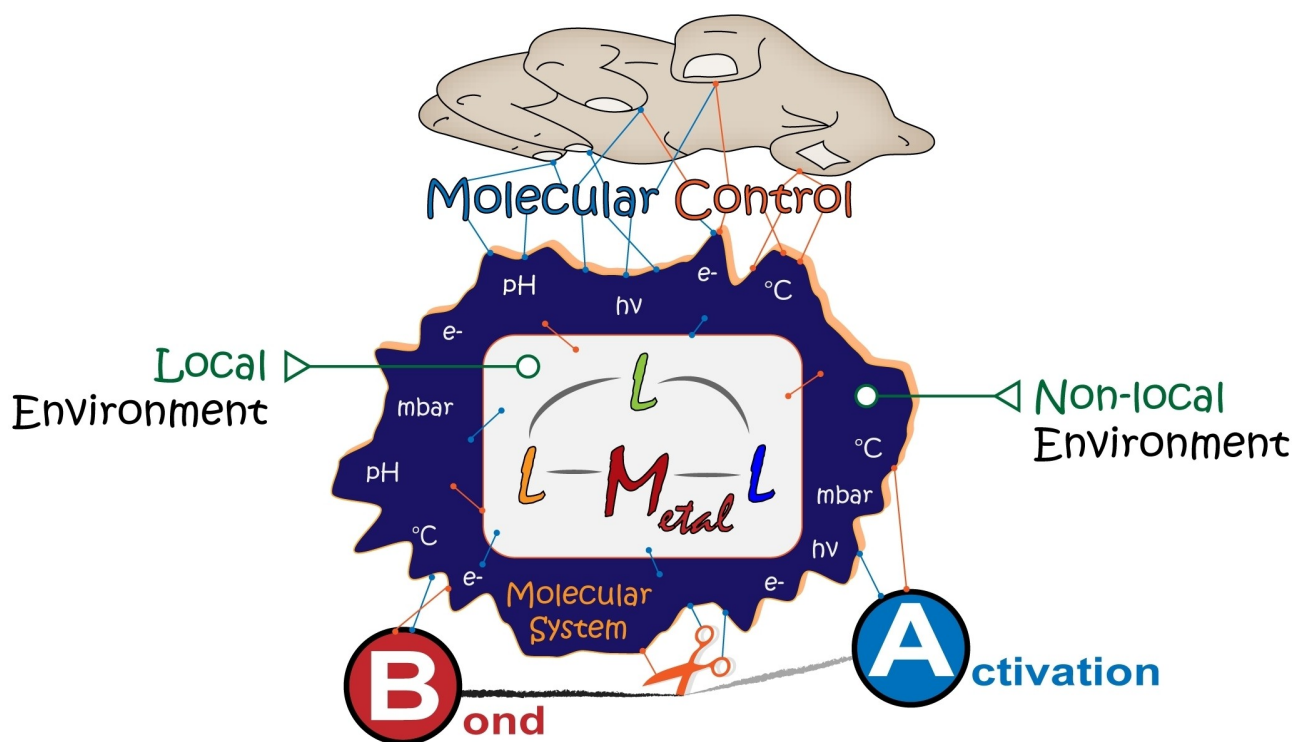


Molecularly Controlled Catalysis – Targeting Synergies Between Local and Non-local Environments

Basujit Chatterjee,^[a, b] Wei-Chieh Chang,^[a, b] and Christophe Werlé*^[a, b]



Future chemicals should preserve the efficiency of their function while reducing hazards and waste. In this context, catalysis – a fundamental pillar of *Green Chemistry* – is still the most effective technique capable of meeting societal requirements while offering sustainability. To further push the boundaries of catalysis and respond to these challenges, a clear understanding of the molecular level interactions is essential. To succeed, we believe it is necessary to consider the transition metal

catalyst as a molecular system encompassing a local and non-local environment. The synergistic effects that are taking place between the ligand, the metal center, and their surrounding environments primarily determine the efficiency of the bond making and breaking processes. This Concept provides tools for identifying, implementing, and combining these effects to control catalysis directly at a molecular level.

Introduction and Background

Chemistry plays an essential role in sustaining the global economy and underpinning future technologies. Modern chemical sectors rely mainly on fossil fuels to provide either energy or primary chemical resources and, therefore, impact the environment.^[1] For this reason, chemical processes are under constant scrutiny. Performance alone is no longer the only requirement; instead, sustainable performance has become a primary goal for the chemist. There is a need to establish a sustainable system to reduce the energy intensity of industrial chemical processes and their impact on the environment.^[2] In this context, catalysis – a fundamental pillar of *Green Chemistry* – is still the most effective technique to bridge requirements and sustainability. However, the quest for chemically efficient syntheses of valuable compounds with recovery and reuse of catalysts, lower waste production, and minimal physical separations remains a significant challenge for homogenous catalysis. Therefore, it is necessary to develop molecular catalysts with optimum adaptability, efficiency, modularity, selectivity, and sustainability. This task becomes even more challenging when the protocols aim at activating and converting small molecules (e.g., H₂, O₂, H₂O, CH₄, CO, CO₂, N₂, NH₃) into elementary building blocks (i.e., H, O, C and N) for their direct application in the synthesis of value-added fuels and basic chemicals.^[3] The undeniable potential of molecular catalysts for the activation of various small-molecules prompted scientists worldwide to investigate further. For a long time, the spotlights were placed on the transition-metal itself – the reactivity occurs at the metal center. In this approach, the ligands are regarded as spectators, which remain unchanged throughout the lifetime of the catalyst.^[4] Since the number of metal/ligand combinations are limited, a paradigm shift was necessary. Comparatively, nature flourishes with unique modes of bond activations,^[5] for which the efficiency of a specific transformation strongly depends on the delicate interplay between local and non-local environments of the transition metal. As a result, considerable attention

has been paid to develop active ligand backbones (i.e., local environment). Cooperative or synergistic effects are the terminologies used to describe ligands acting together with their metals.^[6] These concepts have led to a plethora of developments, among others in bond activation, storage, and transfer of functionalities or in the stabilization of reactive intermediates. Besides the local environment, the catalytic behavior of a transition metal also strongly depends on the reaction conditions (e.g., solvent, temperature, pressure, wavelength, applied potential), which serve as non-local environments. Often, the approach is to empirically combine several of these factors, which has the disadvantage of preventing the identification and implementation of synergistic effects (Scheme 1). We believe instead that it is necessary to consider the transition metal catalyst as a **molecular system** constituted of (1) the transition metal, (2) a local environment (e.g., cooperative ligand), and (3) a non-local environment (e.g., reaction parameters, external electronic stimulus). In this way, synergies can be identified, implemented, and controlled directly at the molecular level. Without aiming to be comprehensive in the different fields discussed in this article, this is an effort to identify and provide tools to integrate synergistic effects into transition metal systems for a molecularly controlled bond activation and catalysis.

Synergistic Local Environment

In the last few decades, several reports confirmed the importance of the local environment of a catalyst. It is possible through an appropriate design of the ligand framework to support and control the reactivity of the transition metal.^[7] This section aims through selected examples to illustrate these findings and to open perspectives for future developments.

Steric and Electronic Parameters

The quest for improved activity and selectivity of the catalyst strongly relies on developing ligands that sterically and electronically meet the requirements of a particular transformation. For instance, sterically encumbering ligands can stabilize reactive intermediates by forming a cavity around the metal center, offering steric protection to key reactive species. In this direction, Meyer and colleagues showed that sterically protective tris[2-(3-aryl-imidazol-2-ylidene)ethyl]amine (TIMEN^R, R=xylyl (**1a**), mesityl (**1b**)) ligands could stabilize terminal

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Fe(IV) nitride complexes **2** (Scheme 2).^[8] Notably, the generated Fe(IV) nitride species were found remarkably air and moisture stable even at room temperature. This study illustrates the significance of steric protection when manipulating reactive metal intermediates (e.g., carbene, imido, nitrene, oxo); these transient species are the keys to understanding the bond making and breaking reactions, allowing for further optimization of the catalytic cycles.^[9]

Secondary Coordination Sphere

Growing evidence suggests that secondary coordination spheres can profoundly influence various functions, ranging from modulating the properties of the catalyst system to assisting in bond activation processes. Recently, many attempts aimed at including such effects in laboratory protocols.^[10] In this respect, Borovik and coworkers reported a tripodal ligand, incorporating three arms with urea derived functionalities (**3**, Scheme 3).^[10a,b] After coordination, the amide groups have their hydrogen atoms adequately positioned towards the center of the cavity, making them available for hydrogen bond interactions in the secondary coordination sphere. The authors took

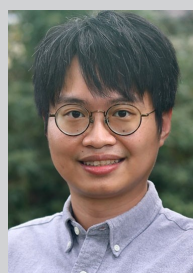
advantage of this structural layout to fabricate a stable iron complex featuring a terminal oxo ligand derived directly from dioxygen (**4**). Inspection of the molecular architecture suggests that the formation of H-bonds with the terminal oxo ligand, in a well-adapted microenvironment, tames the species' high reactivity. Similar terminal Mn-oxo complexes could also be prepared based on this ligand system.^[10b] As illustrated here, an appropriate ligand design can provide a unique balance between *stability* and *reactivity*.

Non-covalent Interactions

Non-covalent interactions can be considered as both local and non-local environments for a molecular system.^[11] They can stabilize a critical transition state and influence the selectivity (e.g., chemo-, regio- or stereoselectivity) of a catalytic process. While the importance of hydrogen bonding – as illustrated in the previous example – is well recognized in catalysis, it is possible to take advantage of other interactions (e.g., coulombic, cation- π , anion- π , π - π stacking, dispersion) in the design of catalytic protocols. An in-depth understanding of these weak



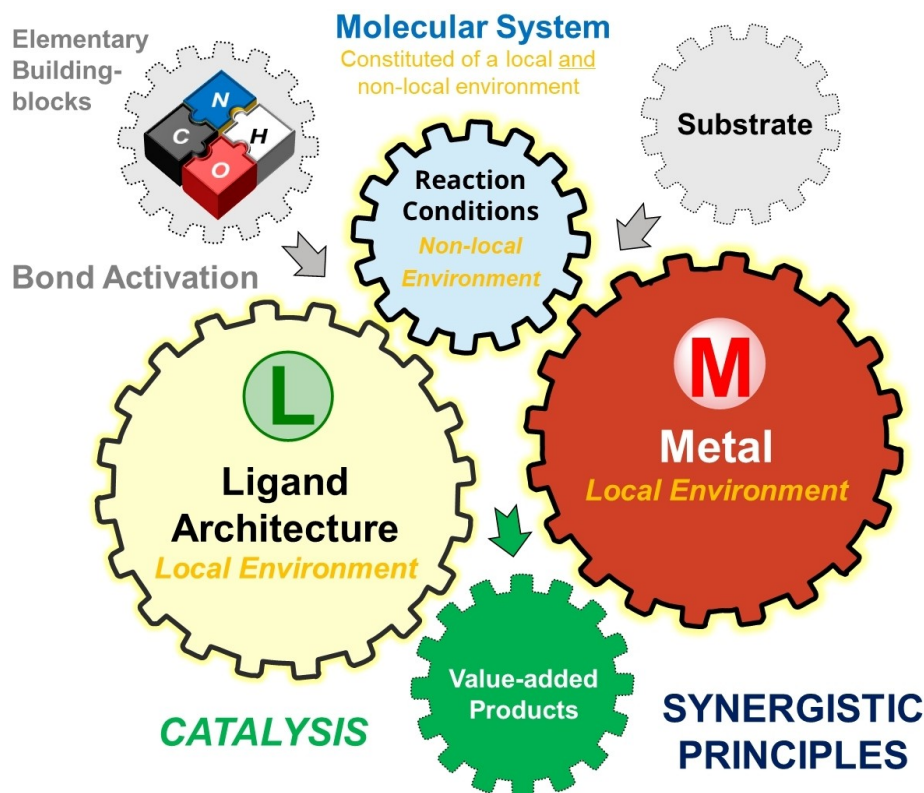
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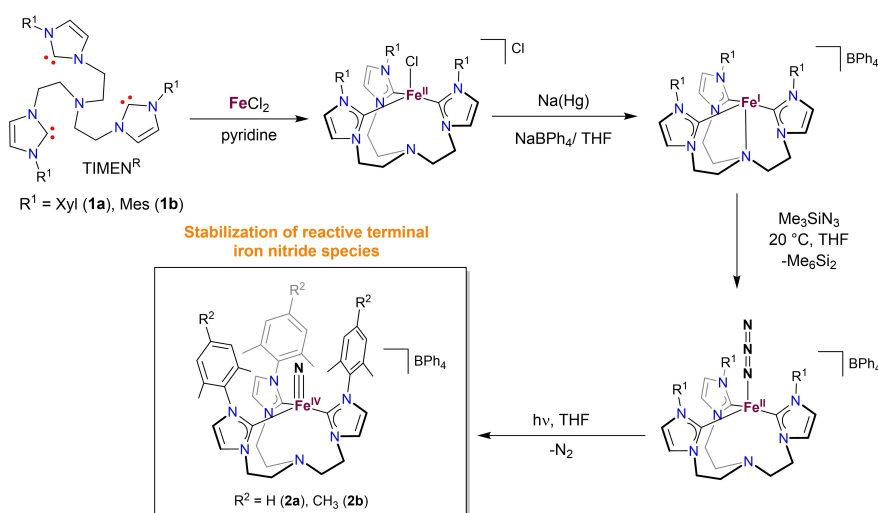
Wei-Chieh Chang obtained his B.Sc. and M.Sc. degrees in Applied Chemistry, respectively, from the National University of Kaohsiung and the National Chiao Tung University. During his Master studies in Prof. Dr. Hsueh-Ju Liu's group, he focused on the synthesis, structural characterization, and reactivity of low-valent heavier group 14 metal complexes. Currently, Wei-Chieh is doing his Ph.D. studies under the supervision of Dr. Christophe Werlé at the Max Planck Institute for Chemical Energy Conversion (MPI-CEC) – enrolled as a Ph.D. student at Ruhr University Bochum. His research focuses on developing polarized transition metal-based systems for atom transfer reactions.



Christophe Werlé is a Max Planck Research Group Leader at the Max Planck Institute for Chemical Energy Conversion, working in collaboration with the Ruhr University Bochum. He leads the independent Max Planck Research Group of Synergistic Organometallic Catalysis. In 2014, he obtained his doctoral degree from the University of Strasbourg (2011–2014). He then served as a postdoctoral researcher, first in the group of Prof. Dr. Alois Fürstner (2014–2016), and then in the group of Prof. Dr. Karsten Meyer (2016–2017). In September 2017, he joined the department of Molecular Catalysis of Prof. Dr. Walter Leitner as Group Leader of Organometallic Electrocatalysis (2017–2019) and began his independent career in September 2019. Research in the Werlé group focuses on developing a molecular-level control of bond activation processes and catalysis via transition metal-based systems.



Scheme 1. Illustration of a synergistic approach.

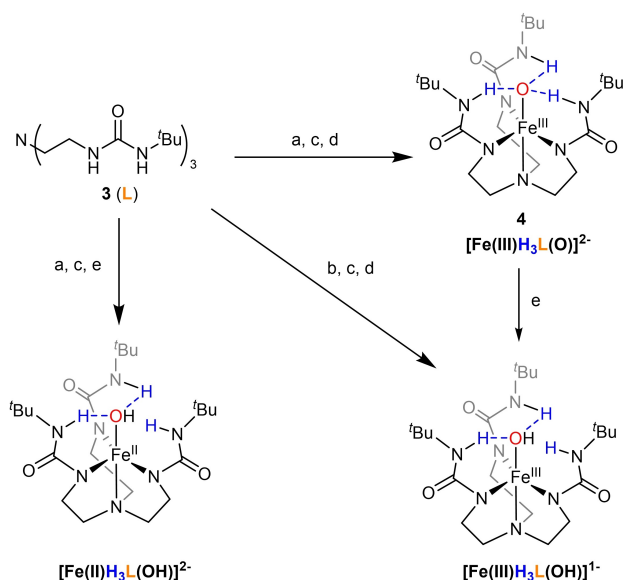


Scheme 2. Sterically encumbering ligands stabilize reactive terminal iron nitride complexes.

interactions and their cooperative mode of action is fundamental to catalyst development.

When non-covalent interactions are involved in a chelate-like binding mode, this is called *Hemichelation* (Scheme 4a); in this way, conformationally flexible and electronically unsaturated metal centers can be stabilized (Scheme 4b).^[12] For example, the reaction of an ambiphilic heteroditopic ligand, such as the tricarbonyl(η^6 -indenyl)chromium anion (5) with a

series of Pd and Pt metallacycles afforded a series of *syn*-facial heterobimetallic complexes **6a–d** (Scheme 4c).^[12b] In these complexes, the metallacycle binds the indenyl fragment via its metal in a η^1 -fashion, leaving the fourth coordination of the chelated metal (M) virtually vacant. Theoretical studies indicated that the formation of these unusual structures is driven thermodynamically by attractive *Coulombic occlusion* of the

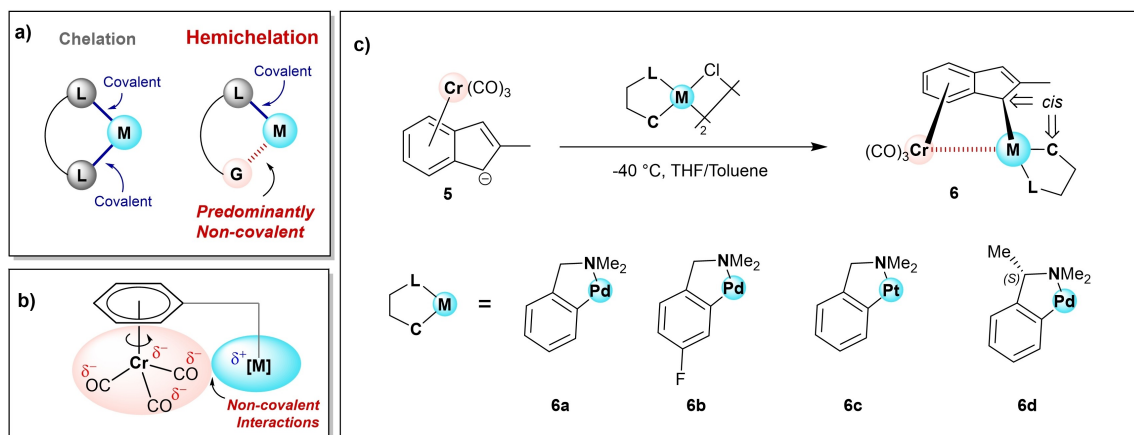


Scheme 3. Formation and stabilization of a terminal iron-oxo species. Conditions: a) 4 equiv. KH, DMA, inert atmosphere (Ar), room temperature; b) 3 equiv. KH, DMA, Ar, room temperature; c) Fe(OAc)_2 , DMA, Ar, room temperature; d) 0.5 equiv. O_2 , DMA, room temperature; e) H_2O , room temperature.

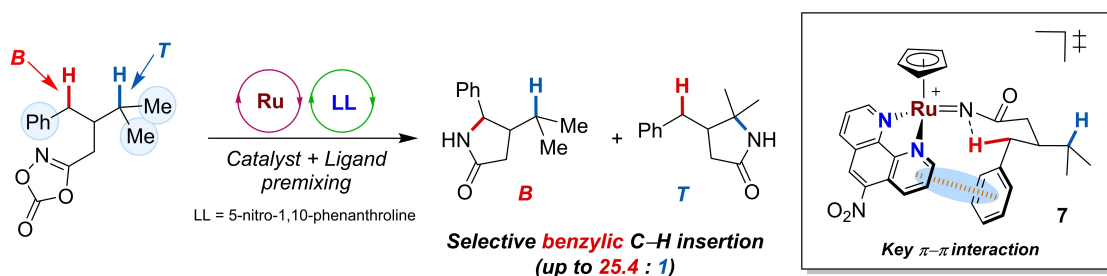
fourth vacant coordination site at Pd/Pt/Rh centers by the Cr(CO)_3 moiety.

In homogeneous catalysis, controlling the site-selectivity of a catalyst constitutes a central theme and can be tailored by non-covalent interactions. This was demonstrated by Baik, Park, Chang, and colleagues in the case of a cationic ruthenium complex **7** exhibiting high selectivity for the amidation of benzylic C–H bonds – over tertiary C–H bonds (Scheme 5).^[13] The selectivity arises from attractive non-covalent interactions between the π -cloud of the polypyridyl ligand in **7** and the π -cloud of an aromatic fragment on the substrate that acts as a formal directing group.

Selectivity is equally significant when preparing polymeric materials, such as biodegradable and biocompatible poly(lactides) (PLA) – contenders to polyolefins in terms of physical and mechanical properties.^[14] In this specific case, the ring-opening polymerization (ROP) of a racemic mixture of lactide (*rac*-LA) may lead to both isotactic PLA (diblock,^[14a,15] or multiblock^[14f,16]) and heterotactic PLA.^[17] Here the ligand architecture, the metal, or the nature of the proximal stereogenic center of the polymeryl group all constitute control parameters that can determine which lactide enantiomer coordinates and inserts. This led to intensive research efforts to identify and design catalysts with high activity, productivity, and selectivity to precisely adjust the polymers' macromolecular features. This led, among others, to the identification of catalytic systems that



Scheme 4. (a) Concept of Hemichelation; (b) Stabilization of hemichelates through attractive coulombic interactions; (c) Synthesis of Cr–Pd/Pt based hemichelates.

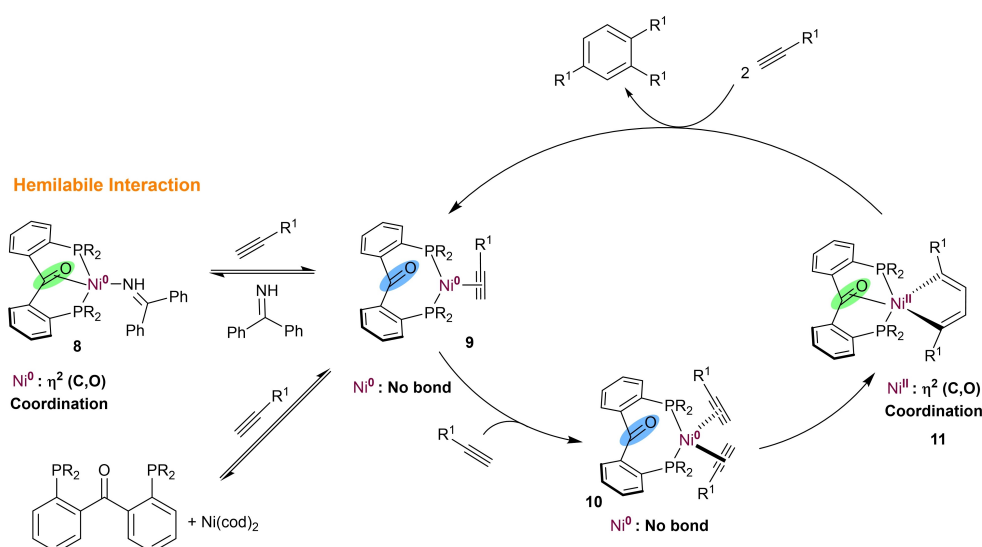


Scheme 5. Pivotal π – π interaction for the site-selective amidation of benzylic C–H bonds.

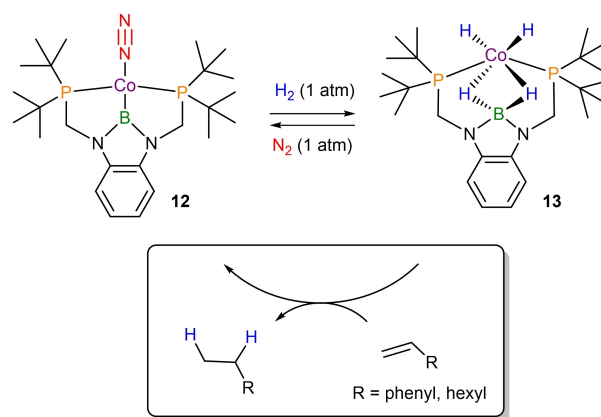
react to external stimuli, allowing temporary switching of polymerization and, therefore, control the properties and compositions of the product.^[18]

Ligand Hemilability

Adaptive hemilabile ligands are polydentate ligands that can adjust their coordination mode by reversibly (de)coordinating the metal center.^[19] They can unveil a masked coordination site and stabilize reactive intermediates by adapting their binding mode throughout the reaction. In this direction, Moret and colleagues investigated nickel-based systems featuring 2,2'-diphosphinobenzophenones derived hemilabile ligands in the [2+2+2] cyclotrimerization of terminal alkynes to produce 1,2,4-substituted benzenes (Scheme 6).^[20] Notably, closely related bi- and tridentate phosphine-based nickel catalysts showed inferior catalytic activities. NMR spectroscopy and DFT studies suggested that the hemilability of the C=O unit eases substrate binding and assists in the key oxidative coupling step. The resting-state **9** can be generated either by ancillary ligand exchange from **8** or *in situ* by combining the anchoring ligand with Ni(cod)₂. Notably, the ketone functionality in **9** is not bound; this facilitates second alkyne coordination and provides **10**. In the next step, a C–C oxidative coupling occurs, with concomitant coordination of the hemilabile ketone to nickel in a η^2 -fashion. It is supposed that this specific interaction contributes to the formation of 2,5-disubstituted metallacyclopentadiene **11**. From **11**, insertion of a third alkyne to generate the final product can proceed either through a [4+2] cycloaddition, migratory insertion, or a [2+2] cycloaddition, followed by reductive elimination of the trisubstituted benzene and subsequent ligand exchange to regenerate **9**.



Scheme 6. Assistance of a hemilabile ligand in the catalytic cyclotrimerization of terminal alkynes to 1,2,4-trisubstituted benzenes.



Scheme 7. Reversible addition of H₂ to **12** and catalytic hydrogenation of olefins.

Z-Type Ligands

Implementing Lewis acidic fragments in pincer architectures to generate Z-type ligands emerged as a new paradigm in recent years. This approach enables precise control of the electronic properties and reactivity of a metal.^[21] For example, Peters and Lin developed a bisphosphino–boryl Co-based complex exhibiting a pseudo-square-planar geometry and featuring a Co–B bond (Scheme 7).^[22] Exposure of Co–N₂ complex **12** to a hydrogen atmosphere led to the quantitative formation of cobalt hydride complex **13**. Interestingly, it is possible to regenerate **12** by exposing **13** to N₂ (1 atm). Such reversible H₂ activation can guide the development of activation-storage-utilization sequences in bond activation. Besides, **12** can hydrogenate 1-octene and styrene with 2 mol% of catalyst loading after short reaction times.

Apart from boron, it is possible to consider other elements (e.g., Al, Ga, In, Sb) to construct Z-type ligands.^[21g,23] For

example, Gabbaï and coworkers reported an antimony-based ligand capable of controlling the platinum center's reactivity (Scheme 8).^[23a] First, an anion exchange reaction converts the Cl₂Sb–PtCl core in **14** into an F₃Sb–PtL unit in **15–16**. This modification sharply affects the Pt–Sb bond that switches from covalent and apolar (**14**) to polar covalent (**15–16**). According to the extreme of the dative formalism, this interaction can be seen as a Pt(0)→Sb(V) interaction delivering a rather electron-rich platinum center with low electrophilicity. Subsequent fluoride abstraction from the diaryltrifluorostiborane moiety in **15–16** leads to the formation of cationic species **17–18**, featuring a highly Lewis acidic diaryldifluorostibonium fragment. In **17–18**, the Sb center exhibits improved σ -accepting properties, which results in an increased Pt→Sb interaction. Thus, the platinum center becomes sufficiently electrophilic in **17** to be able to catalyze enyne cyclization reactions.

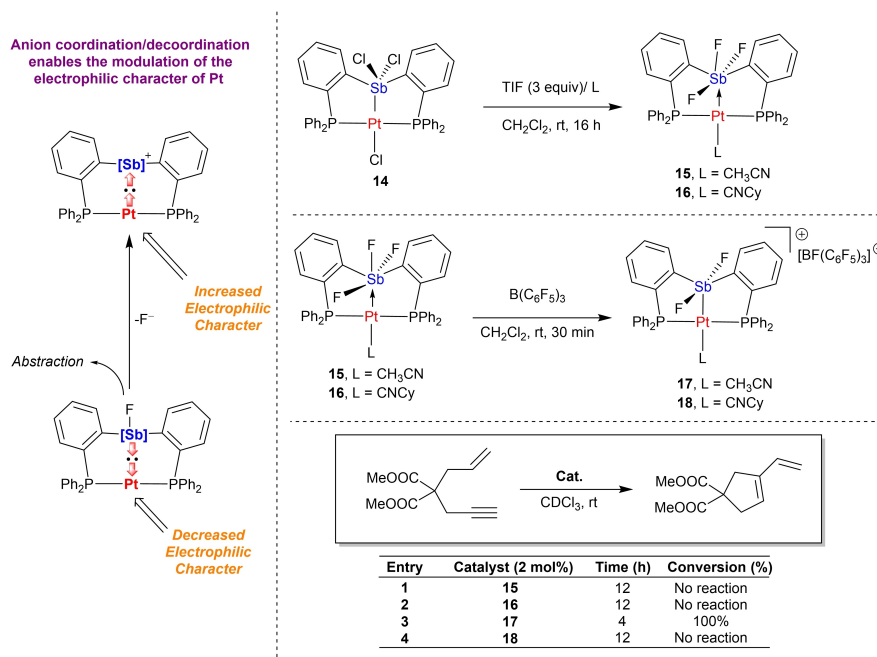
Redox-active Ligands

While noble metals often favor two-electron redox changes – to promote bond-making and breaking events – base metals usually go by one-electron redox changes. This constitutes a major obstacle in replacing the former with the latter as it brings additional challenges for controlling the reactivity of the complex or maintaining the function of the catalyst. In this regard, redox-active ligands have been recognized in coordination chemistry to facilitate and manage redox-events, offering new prospects to noble, base, and main-group metals.^[6k,24] These electron reservoirs engage with their metal by storing and releasing redox-equivalents generated or required during

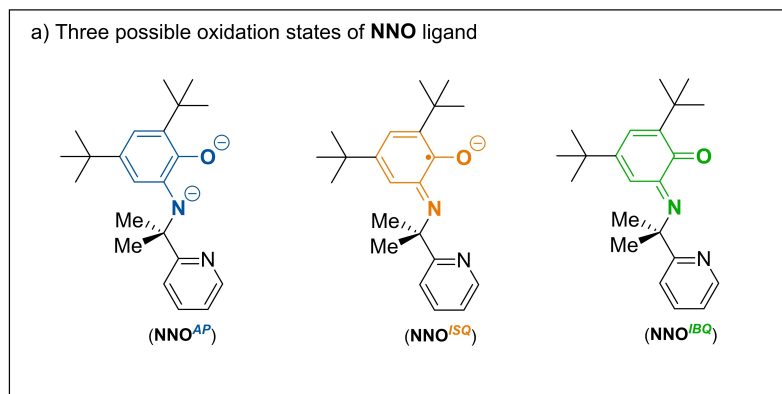
bond activation, and may result, as a possible price to pay, in an increased vulnerability of the ligand architecture.

Recent developments considered redox-active ligands as ligand-to-substrate single-electron transfer platforms.^[24m] Such an approach offers a new strategy for single-electron transfer-induced catalysis.^[25] This has the advantage of (1) preventing the formation of free organic radicals that usually lead to chemoselectivity issues,^[26] (2) circumventing the quest for suitable redox-active metals that can facilitate the desired one-electron transfer to the substrate – as typically encountered in metalloradical-based catalysis.^[27]

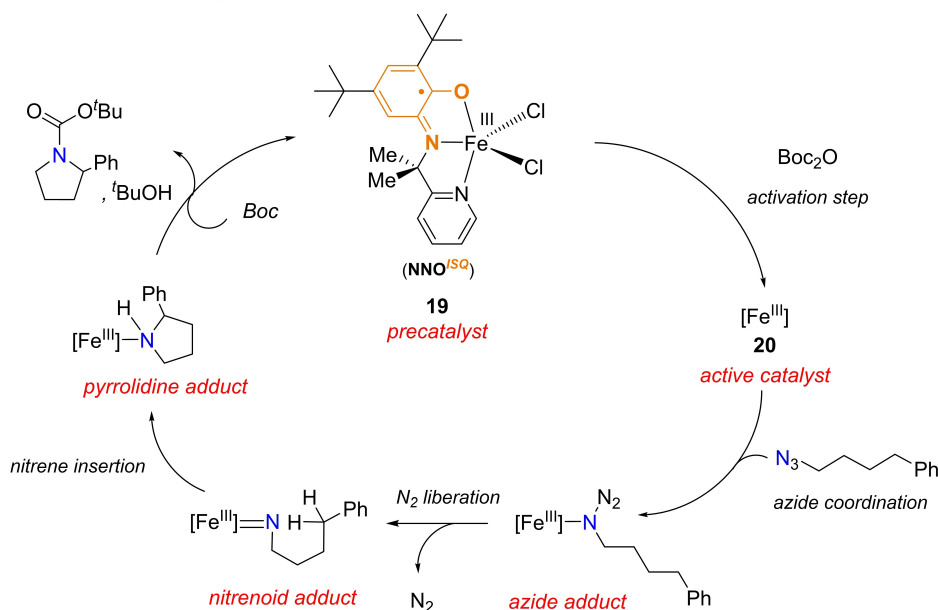
Following the ligand-to-substrate single-electron transfer strategy, van der Vlugt, de Bruin, and coworkers reported an iron(III) complex (**19**) supported by a redox-active pyridine–aminophenol (NNO) framework for the direct C(sp³)–H amination of unactivated organic azides, producing various saturated N-heterocycles with turnover numbers up to 620 (Scheme 9).^[28] This ligand archetype ingeniously combines pincer platforms with the redox-chemistry of aminophenols^[24e,29] and exhibits, as depicted in Scheme 9a, several possible oxidation states.^[30] Experimental and computational studies suggest that complex **19** is best formulated as an iron(III) center that is antiferromagnetically coupled to a ligand-centered NNO^{5Q} radical. Based on experimental observations, the authors proposed a reaction mechanism involving the activation of the catalyst by Boc₂O, generating cationic complex **20** that then undergoes a cationic azide activation route (Scheme 9b). The authors also showed that it is possible to quantitatively recycle iron(III)-complex **19**, permitting its reutilization without loss of catalytic activity. The extreme complexity of the system involving various redox states and spin states for the combination of iron, NNO ligand, and a



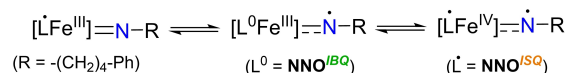
Scheme 8. Modulation of σ -accepting abilities of an Sb-based Z-type ligand.



b) Postulated cycle for the C–H amination of organoazides



c) Possible electronic structures of the nitrenoid adduct:



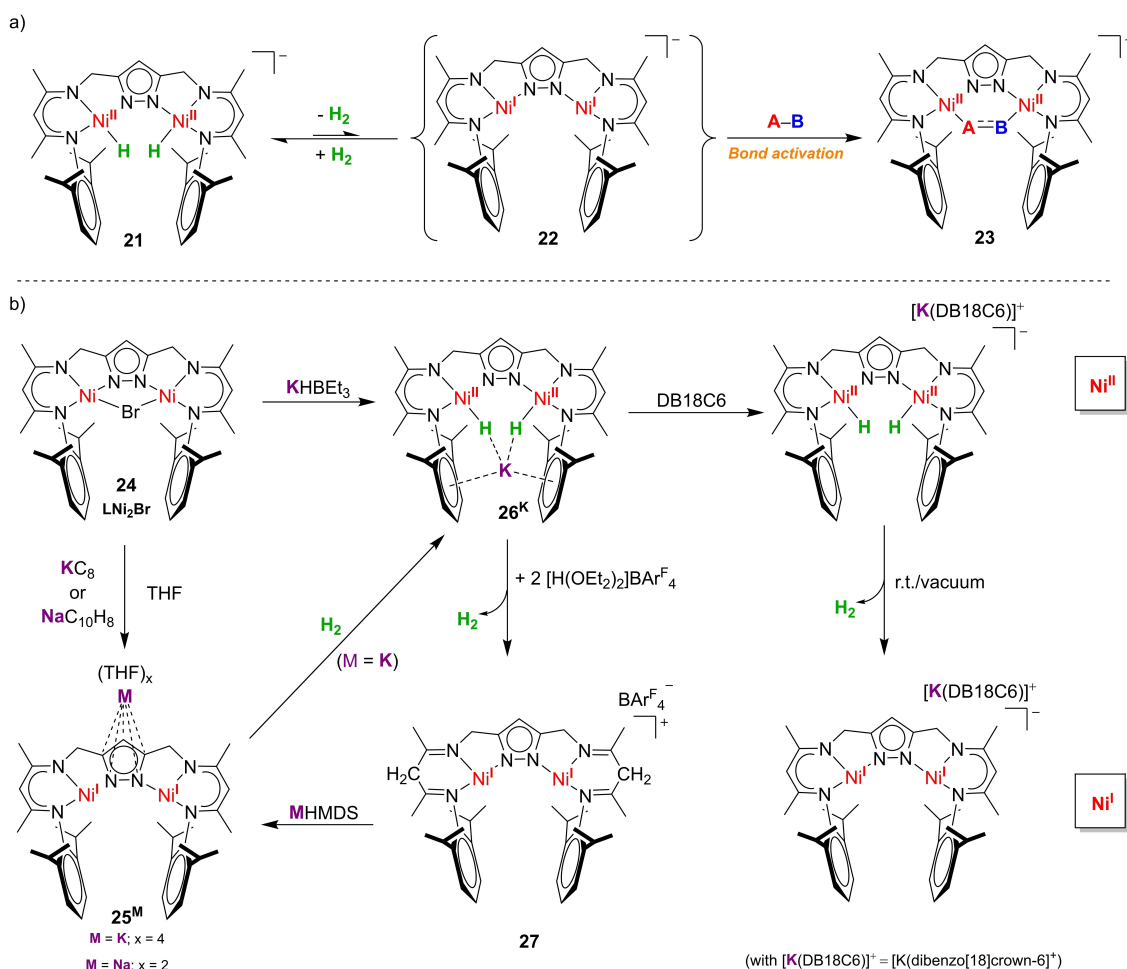
Scheme 9. a) Possible oxidation states of the NNO ligand framework. b) Postulated cycle for the C–H amination of 4-phenylbutyl azide with precatalyst **19**. c) Possible electronic structures of the nitrenoid adduct.

metal-bound nitrene moiety – all of which are potentially redox-active – has to date precluded detailed in-depth spectroscopic and computational analyses.

Influence on Valence, Oxidation Number, and Formal Charge

Ligand environments such as N-Aryl substituted β -diketiminato (nacnac) frameworks have demonstrated a propensity to support reactive metal centers in various oxidation states.^[31] This architectural backbone ingeniously combines design elements (e.g., peripheral aryl substituents) that can be readily modified to stabilize reactive species.^[31c] This strategy was, for

instance, successfully exploited in nickel(I) chemistry.^[32] Notably, dinucleating architectures comprising two β -diketiminato units have also been developed and used in metal–metal cooperativity.^[33] Meyer and coworkers recently introduced a related trianionic dinucleating ligand $[\text{LiPr}]^{3-}$ constituted of a central pyrazolate core that bridges two β -diketiminato fragments.^[34] In the corresponding dinickel(II) dihydride complex **21**, the two-terminal hydrides are oriented into the bimetallic cavity (Scheme 10). For this species, the intramolecular reductive H_2 elimination features low barriers that are influenced by the nature of the cation (i.e., Na^+ , K^+ , or $[\text{K}(\text{dibenzo}[18]\text{crown-6})^+]$). Complex **21** constitutes a masked form of a dinickel(I) species (i.e., in **22**) capable of undergoing



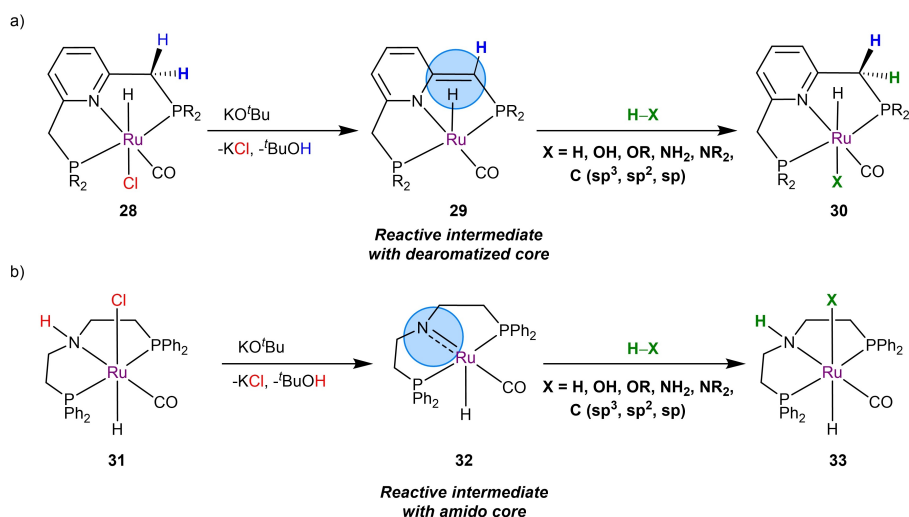
Scheme 10. Protonation of the ligand framework induces H₂ release from 26^K to provide dinickel(I) metalloradical 27.

pairwise H₂/D₂ exchange.^[34a] Besides, **21** can also reductively activate diverse small-molecule substrates A–B (e.g., O₂,^[34b] NO,^[34c] PhNO,^[34d] HCCPh^{[34a)}) resulting in **23** (Scheme 10a). In contrast, when the pyrazolate-based bis(β-diketiminato) ligand features bulky *m*-terphenyl substituents, a reversible 2-electron C–H reductive elimination/oxidative addition chemistry of the phenyl C(sp²)–H bond to the dinickel(I) intermediate occurs *via* metal–metal cooperativity.^[35] Because of this process's reversibility, a powerful 2-electron reductant can be unmasked and react with substrates such as benzaldehyde. In another related study, the authors could isolate the moderately stable dinickel(I) complex featuring two adjacent T-shaped metalloradicals **25^M** (Scheme 10b).^[36] Such pincer-based T-shaped nickel(I) metalloradicals represent powerful reductants capable of bond activation.^[37] Furthermore, the present system provides a highly preorganized dinuclear variant of these species. The authors remarkably demonstrated that in dihydride complex **26^K**, the dehydrogenation process could be controlled by protonating the peripheral ligand with [H(Et₂O)₂]BARF₄ leading to **27**. Such a manipulation drastically lowers the barrier for H₂ reductive elimination. Taken together, these studies unveiled the propen-

sity of these species for metal–ligand cooperation and indicated possible applications in 2e[−]/2H⁺ transformations.

Cooperative Pincer Ligands

Pincer complexes such as **28** can, in the presence of a strong base (e.g., KO^tBu, KOH), be deprotonated at the methylene arm, generating a dearomatized intermediate (**29**, Scheme 11a).^[6i,p] This reactive species can then – *via* Metal–Ligand Cooperation (MLC) – activate small-molecules (e.g., H–X; X=H, OH, OR, C (sp³, sp², sp), NH₂, NR₂). The overall process results in a heterolytic bond cleavage with rearomatization of the pyridine ring. Similarly, the deprotonation of the amino group of a MACHO-ligand furnishes a reactive entity **32** capable of undergoing bond activation. Here also, the protonated amine is regenerated after the activation process (Scheme 11b).^[38] Besides, these ligand systems, due to their high flexibility, can accommodate several coordination geometries without changing the formal oxidation state of the metal center, thus allowing new reactivities.^[6a,c–h,j,39]

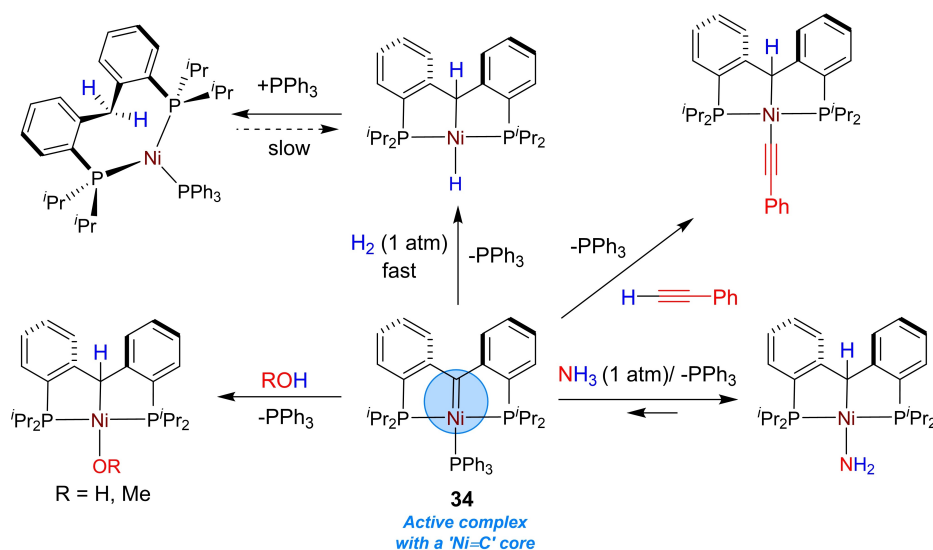


Scheme 11. Small-molecule activation via metal-ligand cooperation. a) MLC involving an aromatization-dearomatization channel; b) MLC involving an amine-amide route.

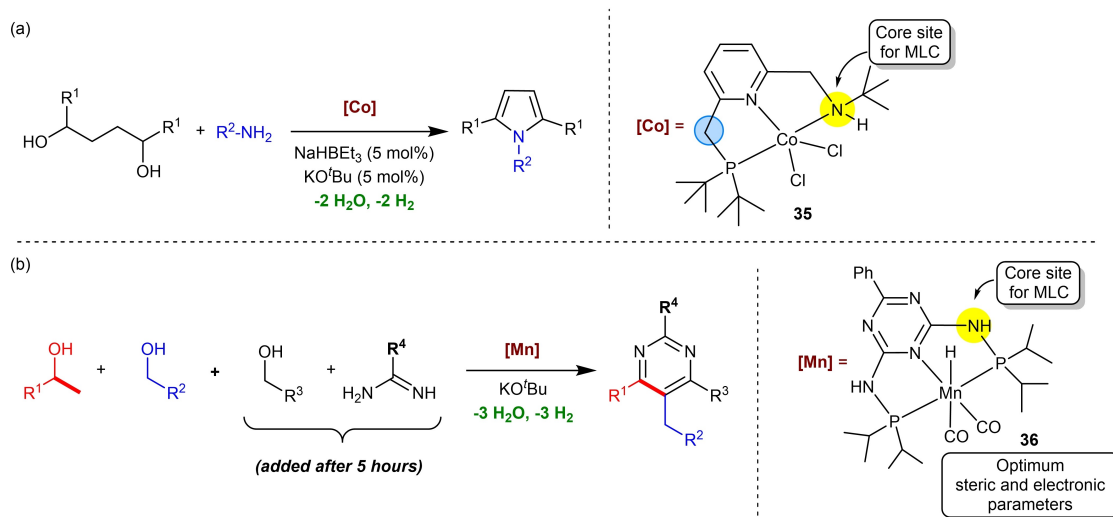
A similar reactivity pattern has been demonstrated for $\text{PC}_{\text{carbene}}\text{P-Nickel}$ complex **34**, which can also activate diverse small-molecules (e.g., H_2 , NH_3 , ROH , PhCCH) through MLC (Scheme 12).^[40] In this system, the reactive nickel-carbene core initiates the bond activation process by heterolytic cleavage. Notably, the high σ -donating character of the central carbon moiety stabilizes the ligand located in *trans* position.

Recent MLC reports have shown a growing interest in utilizing modular ligand platforms combined with environment-friendly metals (Scheme 13).^[41] In the following example, Milstein and coworkers demonstrated a Co-catalyzed (**35**) dehydrogenative coupling of diols and amines, leading to 1,2,5-substituted pyrroles (Scheme 13a).^[42] The overall reaction significantly reduces the number of steps commonly required for pyrrole synthesis. Furthermore, this protocol has the advantage

of only generating water and hydrogen gas as by-products. Along the same lines, Kempe and coworkers reported a manganese-catalyzed one-pot multicomponent synthesis of pyrimidines (**36**, Scheme 13b).^[43] This process involves an earth-abundant Mn-based catalyst. Consecutive addition of the substrates in a one-pot manner under optimized conditions offered the desired products in high yields. In both cases, catalytic amounts of a base are necessary to activate the core site for MLC. In the absence of base, these reactions cease to operate.



Scheme 12. Examples of bond activation processes resulting from synergies between a non-innocent (carbene) ligand and a Ni center.



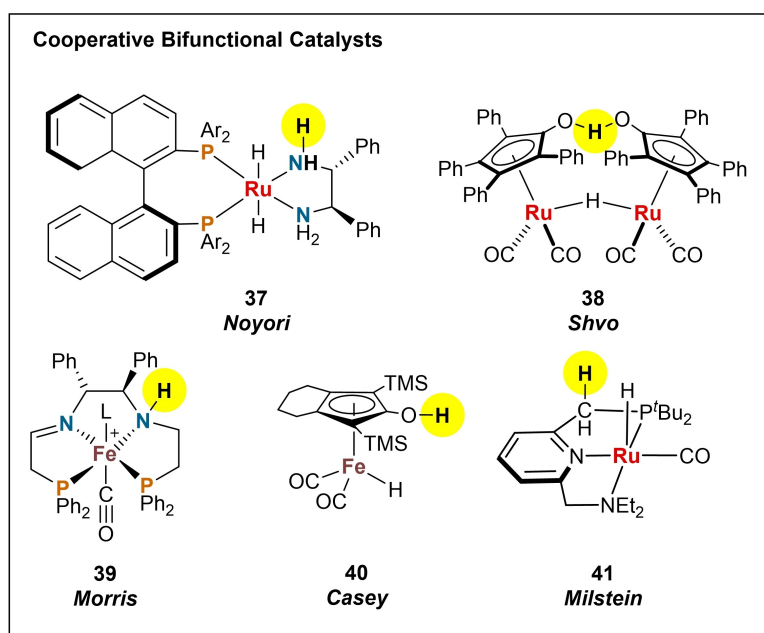
Scheme 13. Synergistic effect between ligands and base metals for multicomponent syntheses.

Molecular Control of Metal-ligand Cooperation

The cooperation between a metal center and an intramolecular Lewis base functionality embedded within the ligand framework has extensively been applied in bond activation. Catalysts by Noyori (37),^[6b,44] Shvo (38),^[45] Morris (39),^[46] Casey (40)^[47] and Milstein (41)^[48] have found numerous applications in both academic research and industrial settings (Scheme 14). To date, the ruthenium-catalyzed asymmetric hydrogenation of ketones^[49] and the rhodium-catalyzed asymmetric hydrogenation of olefins^[50] are among the most efficient artificially and homogeneously catalyzed reactions. In these cases, the tar-

geted products can be obtained in remarkable optical purities – nearing 99.9% enantiomeric excess – with turnover numbers up to 10^4 – 10^6 . Specifically, the Noyori-type catalyst takes advantage of N–H moieties incorporated in the metal center's vicinity as crucial structural design elements.

Traditionally, the amino group attached to the metal center was believed to participate in the catalytic process by donating and accepting H^+ atoms. As a separate phenomenon, it has been recognized that the presence of a Lewis acid can promote (de)hydrogenation catalysis.^[51] For example, in the case of Noyori-type catalysts, Chen and Hartmann showed that substituting the N–H proton by a Lewis acidic alkali metal (e.g., Li^+ ,



Scheme 14. Archetypes of M/OH, M/NH, and M/CH cooperative bifunctional catalysts.

Na^+ , K^+) might assist, together with an alkoxide fragment of the basic promotor, in the cleavage of the H_2 molecule bound to ruthenium.^[51a] In related studies, Dub and coworkers further shed light on the N–H group (or N– M_{alkali} as a result of its reaction with an alkali metal) and described its decisive role in stabilizing rate-determining transition states by non-covalent N–E...O interactions (E=H or M_{alkali}).^[52] Therefore, it transpires that N–X bonds may not be cleaved or formed in catalytic cycles as much as initially thought.

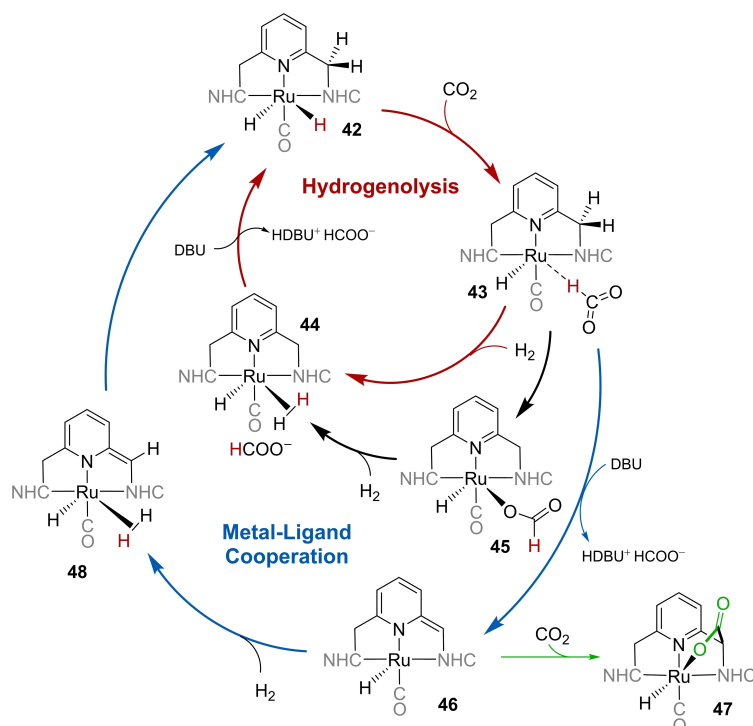
In related studies, de Bruin and coworkers have also reported a non-direct role of the amido moiety for ruthenium-catalyzed methanol dehydrogenation reactions.^[53] DFT calculations, in this case, suggested that the amido moiety of the catalyst remains permanently protonated under operative conditions. The N–H group was found to act as a supramolecular cooperative directing group, facilitating substrate/solvent orientation by H-bonding. Another essential aspect is the discovery that solvent molecules participate in crucial mechanistic steps by impacting reaction barriers. This example illustrates the importance of implementing a molecular description of the solvent as a non-local environment to accurately and realistically describe the reaction pathways. Without diminishing the ligand impact in hydrogenation/dehydrogenation reactions, these studies nevertheless encourage the reader to re-evaluate its overall effect in bifunctional catalysts.

In the case of CO_2 hydrogenation to formate, transition metal systems capable of metal–ligand cooperativity (MLC)^[6p,s,54] are particularly attractive because of their proven efficiency.^[51b,55] Typically, MLC strategies consider the heterolytic

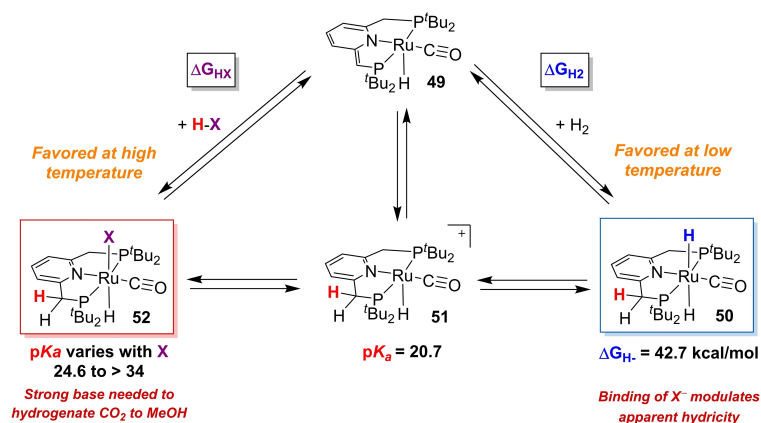
cleavage of H_2 with ligand protonation concomitant to hydride installation on the ruthenium center. For related systems (42), Pidko and coworkers unraveled alternative reaction mechanisms and identified reaction parameters providing control over the catalytic cycle (Scheme 15).^[55g,h,56] Their calculations identified a direct catalytic path, in which the deprotonation of a cationic Ru– H_2 species (44) is mediated by the added base and outer-sphere formate. Their study suggests that in this case, the ruthenium complex with formate bound to the metal center (47) is an off-cycle species in contrast to the MLC pathway. Depending on the reaction conditions, the relative concentration of the reactive species can be controlled. For instance, an increased H_2 pressure drives the reaction towards the dihydrido complex 42.

Saouma and coworkers investigated how the reaction parameters can impact the selectivity and performance of PNP–ruthenium system 49 in CO_2 hydrogenation (Scheme 16).^[57] Even though this catalyst system is known to produce formate using a mild base, in contrast, a strong base can lead to MeOH production. Their in-depth thermochemical analysis provides crucial insights on how the pKa of the base, hydricity of the complex, temperature-dependent equilibrium, and propensity of the dearomatized complex 49 to react with H_2 (to 50) over other H–X species (to give 52; X=OH, OMe, OCHO, OC(O)NMe₂), can provide molecular control over the catalyst and impact the mechanism and outcome of a catalytic cycle.

In computational studies, Pidko and coworkers have also emphasized the importance of alkoxide additives in manganese catalyzed ester hydrogenation.^[58] Apart from the involvement of KO^tBu as the stoichiometric reagent for precatalyst activation,



Scheme 15. Possible catalytic cycles for the hydrogenation of CO_2 to formates by Ru–CNC Pincer complexes (42).



Scheme 16. Thermochemical study of PNP–Ru complex 49 in CO₂ hydrogenation.

the base plays other decisive roles in the catalytic cycle. First, the potassium cation pre-activates the substrate within the complex through secondary interactions, facilitating the critical catalytic hydride-transfer step. Furthermore, the inorganic base promotes hydrogen activation, which is essential for the regeneration of the Mn–Hydride complex. In this reaction, the authors identified the catalyst to operate through an outer-sphere mechanism as the primary catalytic cycle. However, in a competing path, inhibition of the catalyst *via* the formation of a stable Mn-alkoxide constitutes a resting state. Notably, potassium *tert*-butoxide facilitates the hydrogenolysis of this species, contributing to the reactivation of the catalyst. The promoting effect of this specific base on H₂ activation appears to be much stronger than other alkali metals *tert*-butoxides, which is essential for the regeneration of the catalyst from the deactivated state.

These findings and reports help us to refine and expand the early mechanistic picture postulated for these systems and provide a basis for discussing the importance of the reaction parameters and promoters – such as the base – in multifunctional catalytic systems.

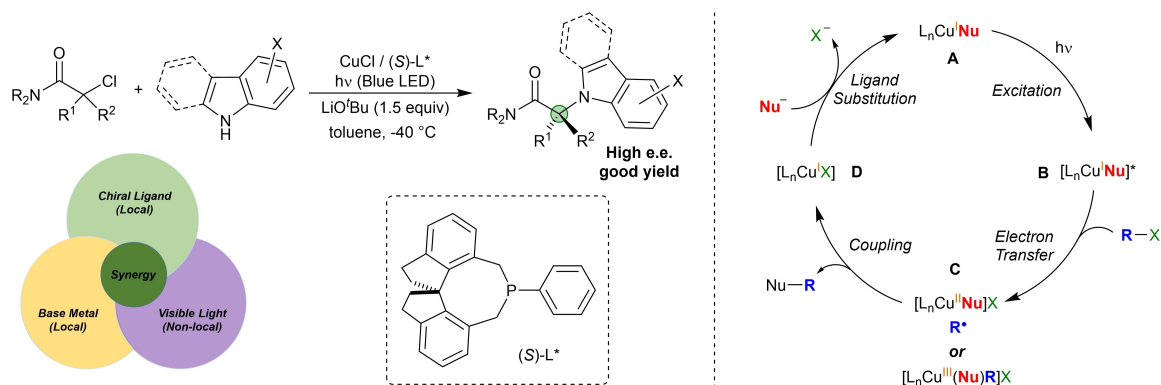
Synergistic Non-local Environment

As illustrated by the examples discussed above, taking advantage of the synergy between a metal and its local ligand environment can provide reactive complexes in a manageable form and lead to efficient chemical transformations. However, the immediate non-local environment is equally important, for it supplies the necessary support to the catalyst to operate appropriately. In the absence of an energy source (e.g., temperature, source of electrons) to activate the catalyst (and the substrate), or an appropriate reaction medium (e.g., acidic, basic), the catalytic process remains incomplete. The synergistic involvement of the non-local environment gives an impulse to the catalyst to run from its maximum efficiency.

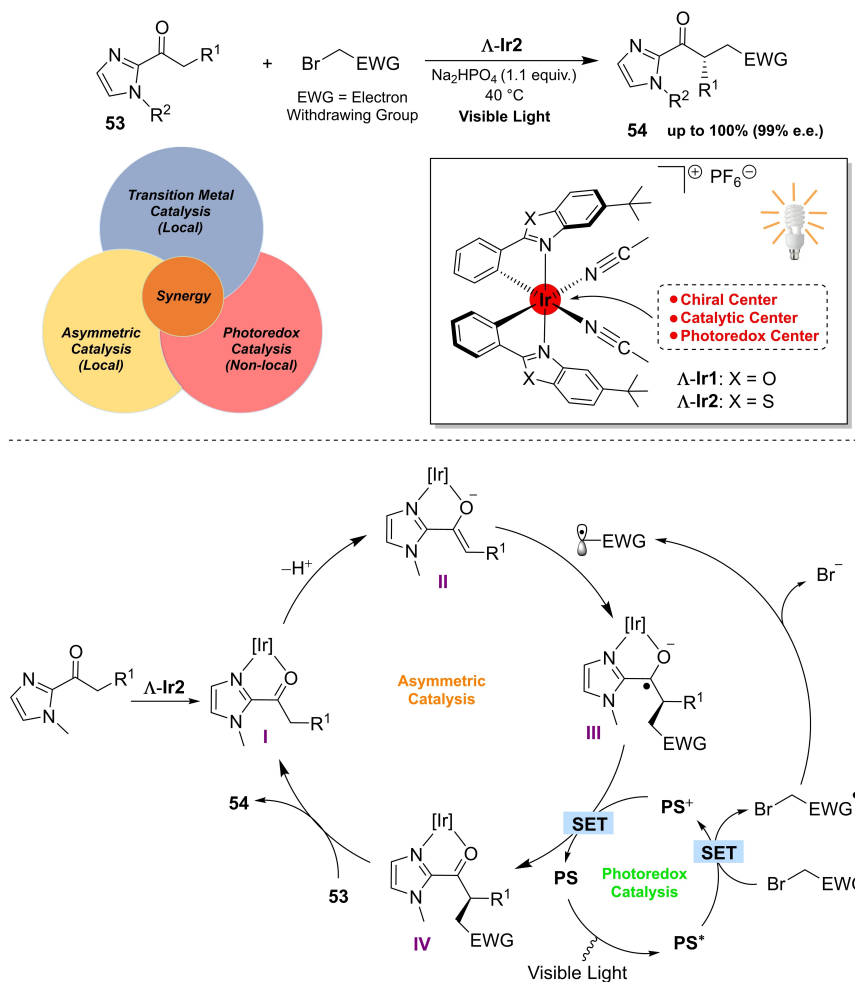
Photochemistry

Accordingly, efforts were made to combine molecular catalysts with renewable resources such as visible light.^[26b,c,59] For example, Peters, Fu, and coworkers showed that a chiral catalyst based on copper could, in the presence of visible light, efficiently perform enantioconvergent C–N cross-coupling reactions of racemic tertiary alkyl chlorides with amines to produce substituted stereocenters in high enantioselectivity (Scheme 17).^[60] This emphasizes that a single catalyst can – under the right conditions – combine: asymmetric synthesis, photochemistry, earth-abundant metal catalysis, and cross-coupling reactions. Such protocols would conventionally require the intervention of several catalysts. Besides, because bioactive molecules are omnipresent, the induction of molecular chirality in the presence of renewable sources will continue to attract considerable attention in the future. The possible mechanism involves the irradiation of a copper-nucleophile complex (A), leading to an excited-state adduct (B). Then, adduct B engages in electron transfer with the alkyl halide (R–X) to provide an alkyl radical. Subsequently, bond formation between the radical and the nucleophile (Nu) occurs to provide the product (Nu–R) through an inner-sphere pathway. Interestingly, in this example, a single copper catalyst is responsible for the photochemistry and the enantioselective bond-forming step.

Also, Meggers and colleagues showed that under visible light, an iridium-based catalyst could perform the enantioselective alkylation of 2-acyl imidazoles (Scheme 18).^[61] In this elaborated asymmetric photoredox system, the metal center simultaneously serves as the sole source of chirality, the catalytically active Lewis acid center, and the photoredox center. The reaction mechanism starts with the coordination of 53 in a bidentate manner to the Ir-catalyst (intermediate I). Next, deprotonation leads to the formation of a nucleophilic Ir(III) enolate complex (intermediate II). Subsequently, the chirality generating step involves the exergonic addition of a photo-reductively generated electrophilic radical to the electron-rich metal-coordinated enolate double bond. This leads to



Scheme 17. Synergy between metal, ligand, and visible light.



Scheme 18. Combination of transition metal, asymmetric and photoredox catalysis into a single molecular platform.

the formation of an iridium-coordinated ketyl radical (intermediate III). Then, oxidation of the ketyl intermediate (III) to the corresponding ketone by single electron transfer (SET) provides the Ir-coordinated product (complex IV) along with the regeneration of the Ir(III) photosensitizer (PS). Finally, product 54 is released from complex IV upon exchange with 53 to start

a new catalytic cycle. The proposed key intermediate of the overall process is the iridium(III) enolate complex II, which elegantly combines the asymmetric catalysis with the photoredox cycle.

The photocatalytic reduction of CO_2 can lead to several platform chemicals, with CO and HCO_2^- being two of the most

commonly observed. It is often assumed that the catalyst is the main factor influencing the selectivity. In order to better understand the origin of selectivity, Delcamp, Papish, and colleagues investigated how the non-local environment (e.g., solvent, electron source, proton source, photosensitizer (PS)) can modulate the product selectivity of ruthenium catalysts **55–56** in the photocatalytic CO₂ reduction (Scheme 19).^[62] Interestingly, when a catalyst was – under one set of conditions – highly selective for CO or HCO₂[–], the authors showed that it could – through non-local environmental modifications – become highly selective for the opposite product while retaining high turnover numbers. The authors also identified that the proton source and the identity of the photosensitizer could influence the product selectivity. Also, water was found to affect the product selectivity drastically and to be crucial for formate production. Oppositely, the nature of the solvent, the sacrificial electron donors, and the catalyst architecture played only a modest supporting role, slightly affecting the selectivity. Importantly, however, the authors observed substantial durability and rate differences based on the solvent choice. This example highlights the importance of carefully considering reaction conditions before ascribing catalyst selectivity to be solely inherent to the catalyst design.

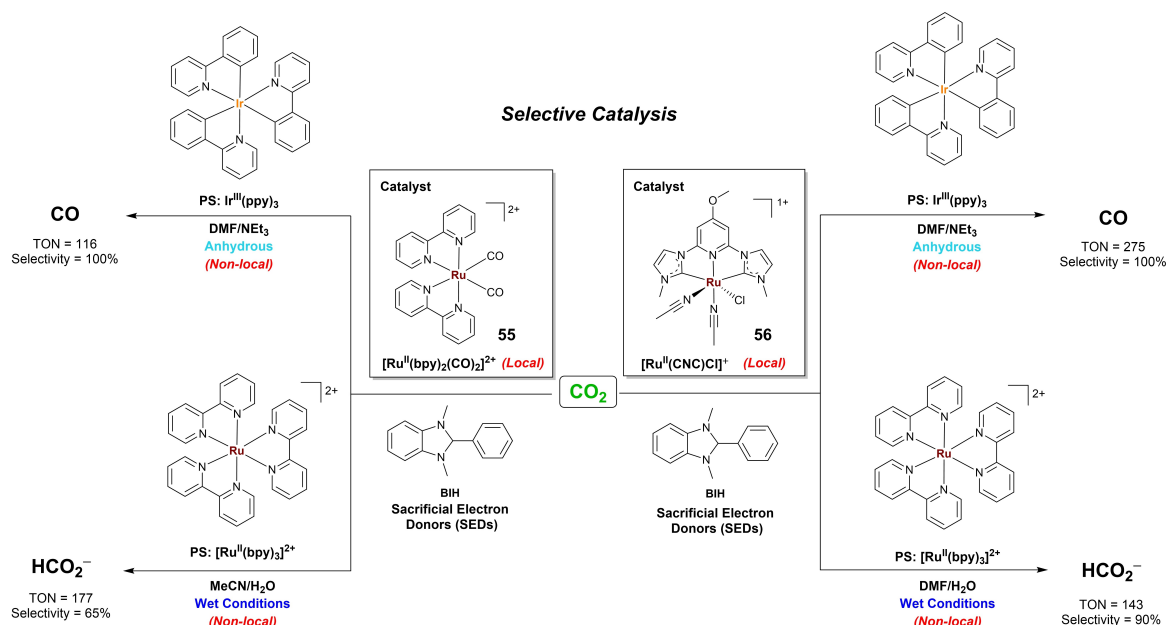
Electrochemistry

Likewise, it is possible to target synergies between a molecular catalyst and electrochemistry (i.e., a green non-local electronic stimulus).^[25i,26a,63] Peters and coworkers reported the electrocatalytic nitrogen fixation catalyzed by a molecular tris(phosphine)borane iron(I) complex (**57**).^[64] The authors found that the pK_a of the acid used for the reaction influences the

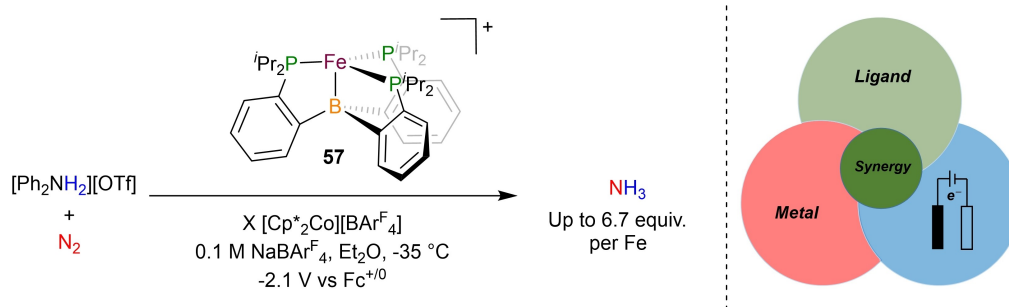
iron catalyst's selectivity for N₂ reduction over side reactions, such as the Hydrogen Evolution Reaction (HER). Moreover, the interaction between the anilinium triflate and the cobaltocene appears to play a significant role. DFT studies indicate that a protonated cobaltocene species, derived from a reaction with anilinium triflate acid, serves as a strong PCET (proton-coupled electron transfer) donor; and thus, contributes to the formation of the N–H bonds. The overall process leads to the complete reduction of N₂, generating up to 6.7 equivalent of NH₃ per Fe catalyst (Scheme 20).

Electrocatalysts incorporating redox-active ligands have also been reported.^[65] For example, Jiao, Zhang, and colleagues demonstrated that both ligand- and metal-centered redox features could be combined in an electrocatalytic cycle (Scheme 21).^[66] The authors showed that a Co(III)-complex bearing a redox-active o-diphenylenedicarboxamido (bpb^{2–}) could act as an electrocatalyst for water oxidation in a neutral aqueous solution (pH=7.0). By increasing the potential, the Na[(L₁^{4–})Co(III)] is – in the presence of water – first oxidized to [(L₁^{2–})Co^{III}–OH] complex *via* a ligand-centered proton-coupled electron transfer (PCET). Next, the resting state [(L₁^{2–})Co^{III}–OH] was further oxidized to a [(L₁^{2–})Co^{IV}–O] complex, which was able to react with H₂O to form the O–O bond in the presence of a phosphate buffer solution. Notably, no catalytic water oxidation behavior was observed for a similar complex with the non-redox active ligand (L₂), indicating that the redox-active ligand L₁ plays a substantial role in this multielectron catalytic cycle.

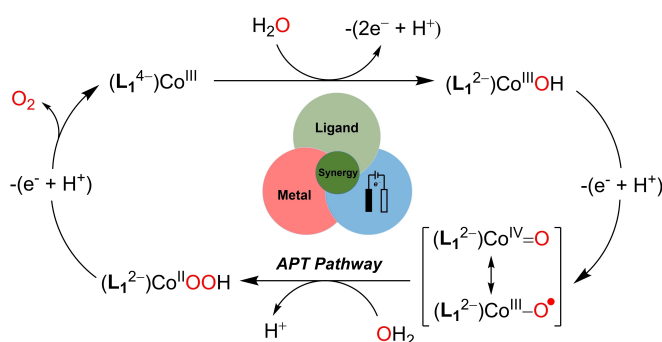
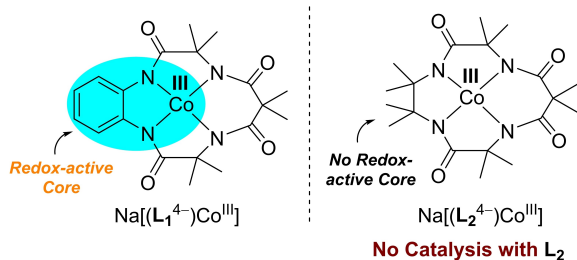
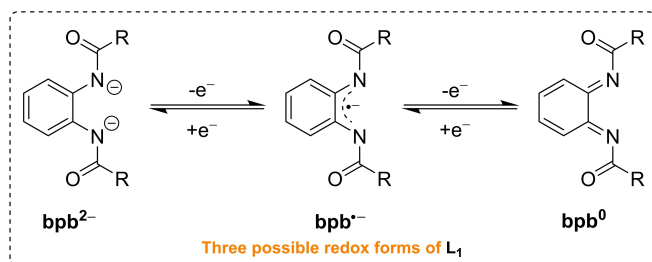
The importance of the non-local environment has also been studied in the context of CO₂ reduction. In-depth mechanistic and thermochemical investigations by Saouma and coworkers in the case of (N[^]N)–Mn system **58** – whereby N[^]N represents a bipyridine (bpy = 2,2'-bipyridine; mesbpy = 6,6'-dimesityl-2,2'-



Scheme 19. Importance of (non-local) reaction conditions on product selectivity.



Scheme 20. The synergy between metal center, ligand and an electron source in nitrogen fixation.



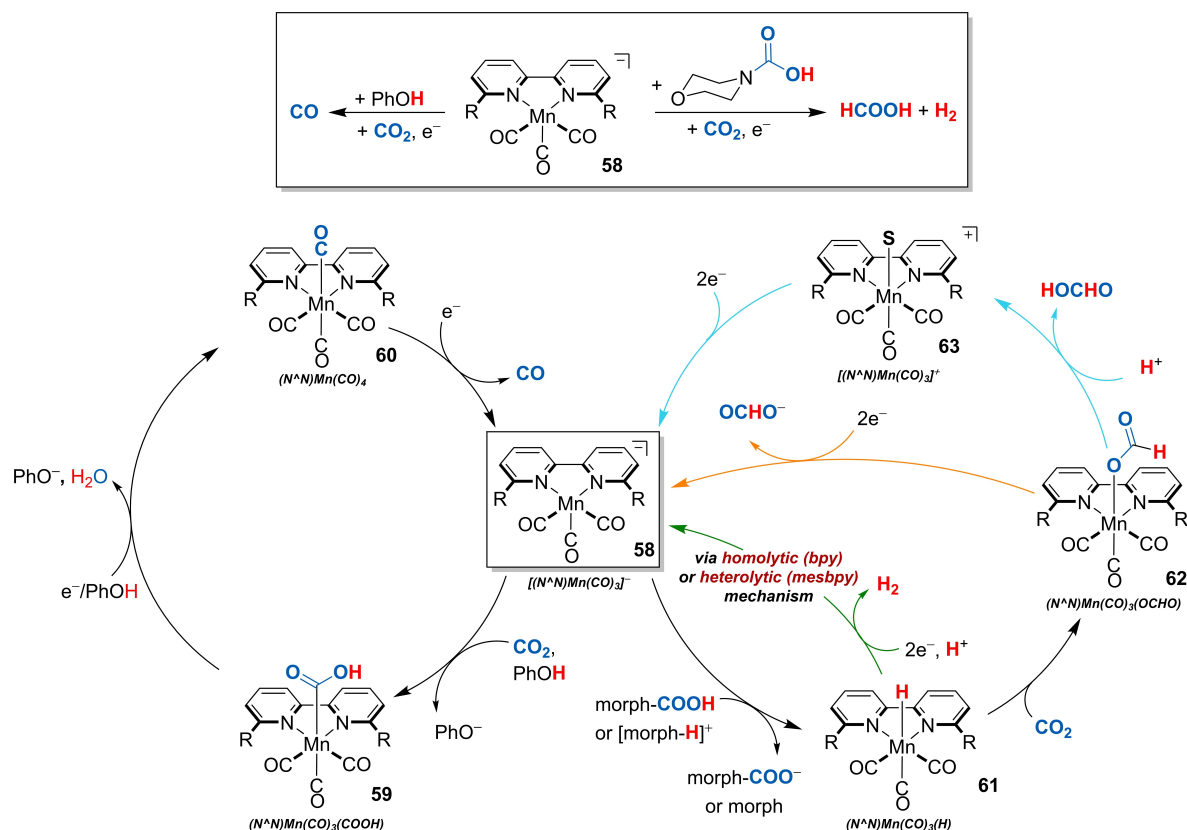
Scheme 21. Synergy between a redox-active ligand, a metal, and non-local parameters.

bipyridine) – shed light on essential catalytic control parameters (Scheme 22).^[67] For instance, the addition of morpholine to the system generates a more acidic environment, allowing for a Mn–H (**61**) to become a kinetically competitive intermediate. This modifies the product selectivity from CO to H₂ and formate. Thermodynamic studies indicated that the hydricity of the Mn–H is not strong enough to reduce CO₂ unless considering formate binding (**62**), which increases the apparent hydricity of the complex. In this system, the steric bulk of the ligand was

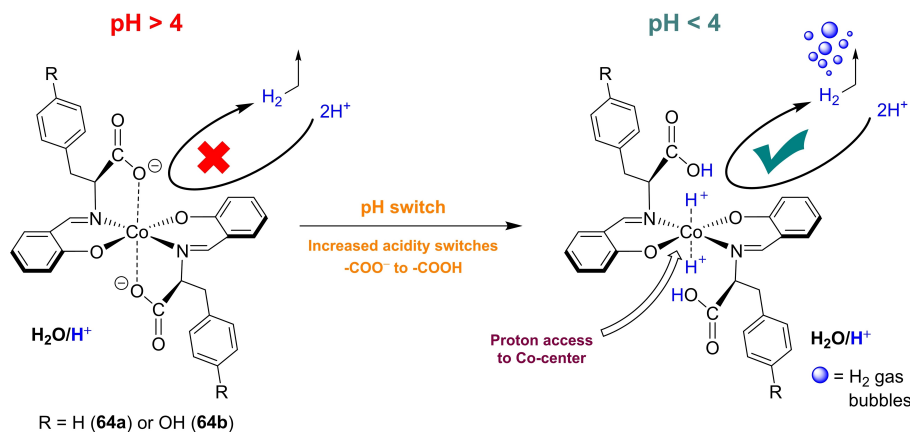
found to influence the product selectivity considerably. Decreasing the steric bulk favors bimetallic H₂ production and supersedes the reaction with CO₂; in this case, H₂ is the dominant product. In contrast, when the bimetallic pathway for H₂ evolution shuts down due to an increased steric bulk, the Mn hydride becomes more stable; subsequently, CO₂ insertion into the Mn–H bond to give a formate species becomes faster than heterolytic H₂ production. The thermochemical analysis helped to identify key parameters affecting the product selectivity. Thus, a clear picture of the mechanism taking place at the molecular level could be obtained, allowing molecular control over the catalytic sequence.

Acid-Base Control

The reactivity of a molecular catalyst can also be controlled based on the pH.^[68] Dutta and coworkers designed Co-based complexes **64** featuring an outer coordination sphere with protic functionalities, such as natural amino acid-derived carboxylic acid and phenolic –OH groups (Scheme 23).^[69] This inclusion rendered an otherwise inactive cobalt-salen-like core active in the electrocatalytic H₂ evolution. Interestingly, this cobalt complex exhibits a unique pH-switchable reactivity. In its basic form (COO[–]) at a pH higher than the pK_a of the carboxylic acid groups (~4.0), the resulting carboxylate functionality acts as an axial ligand. This blocks the protons from accessing the reduced cobalt center, consequently shutting down the catalytic H₂ production cycle. Oppositely, the protonated COOH (at pH below 4.0) constitutes a relatively weak axial ligand. This allows the binding of protons to the electron-rich and reduced cobalt center, which then triggers the H₂ production. Here, the COOH group acts as a proton conduit, thus improving the proton reduction activity of the molecular complex. The phenolic OH group itself can also function as a peripheral functionality supplying protons to generate H₂; however, its influence was reported inferior to the COOH group. Besides, NMR studies suggested that the basic functionalities are involved – in the aqueous solution – in an intricate hydrogen bonding network around the metal center, which considerably controls the efficiency of H₂ production, in terms of both the rate and overpotential requirements. This study shows that by installing pH-responsive functionalities in the metal coordina-



Scheme 22. Proposed reaction mechanisms for the electrocatalytic reduction of CO_2 to CO (left) or formic acid (right). The green arrows show H_2 production, and the stoichiometry relates to the heterolytic route. Light blue arrows indicate direct protonation of $\text{Mn}(\text{OCHO})$, while orange arrows indicate reduction followed by formate loss.

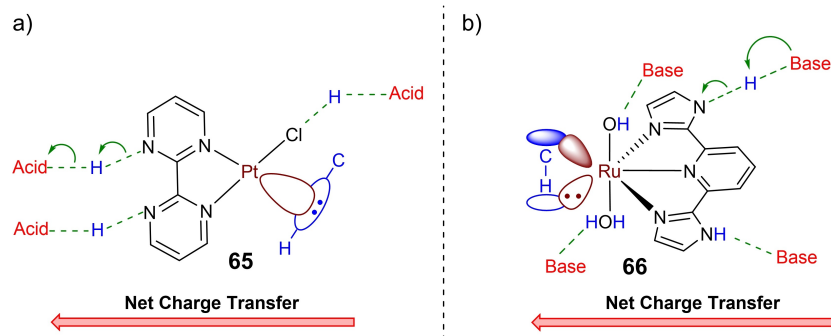


Scheme 23. A pH switchable catalytic H_2 production in the case of Co-based molecular catalysts.

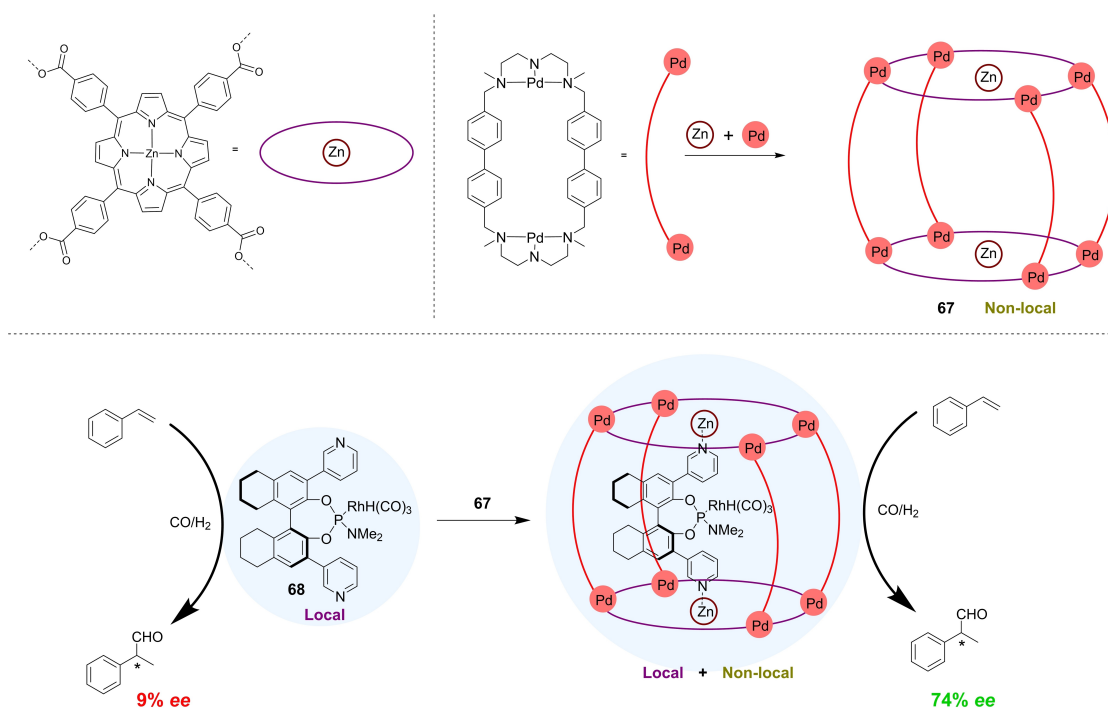
tion sphere (local or non-local), significant improvements in terms of catalytic efficiency can be achieved.

Periana and coworkers have also reported cooperative systems that are dependent on the reaction conditions. They demonstrated that the cleavage of C–H bonds followed a push-pull mechanism, which can be either electrophilic (in the presence of acid) or nucleophilic (in the presence of base). For instance, when considering platinum complex **65**, a strongly

acidic reaction medium protonates the pyridine ligand framework (Scheme 24a).^[70] This removes electron density from the metal and increases its electrophilicity. The resulting lower energy metal-based LUMO can then favorably interact with the low-lying HOMO of the C–H bond, which leads to bond activation. In contrast, for ruthenium complex **66**, basic conditions promote the deprotonation of the ligand and coordination of OH^- ligands to the metal (Scheme 24b).^[71] This



Scheme 24. The synergy between metal, ligand, and reaction conditions. a) Electrophilic and b) nucleophilic cleavage of C–H bonds promoted by an acid or a base, respectively.



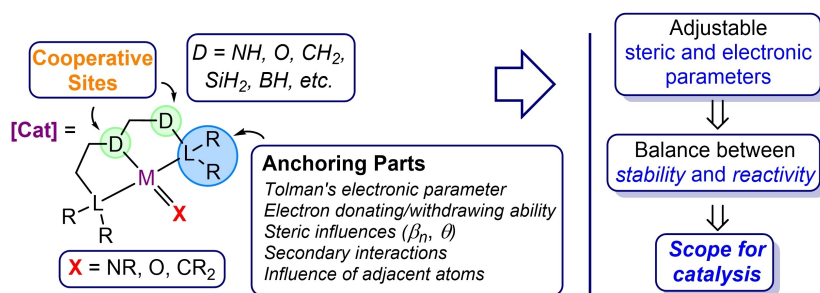
Scheme 25. Encapsulation-driven enhancement of enantioselectivity.

increases both the electronic density and the π -nucleophilicity of the metal by raising the energy level of the metal-based π -donor orbitals (HOMO) that can then interact with the high energy anti-bonding orbitals (LUMO) of the C–H bond, thus activating the bond.^[72] These examples illustrate that there can be a clear dependence of the C–H bond cleavage process based on the nature of the reaction medium.

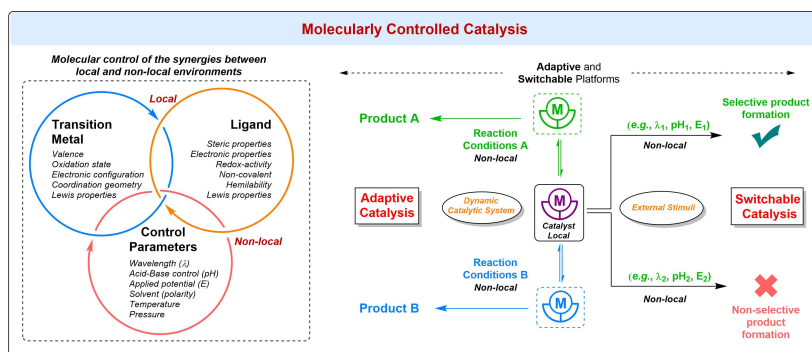
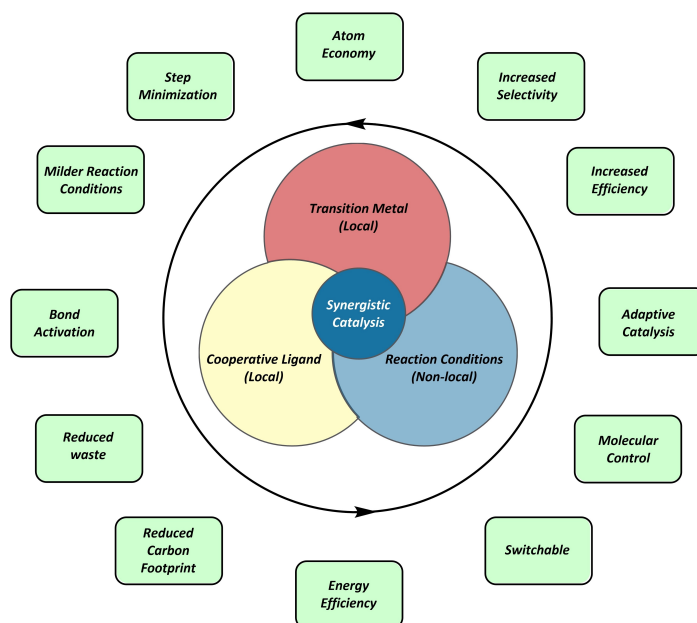
Supramolecular Encapsulation

Embedding a chiral catalyst into a supramolecular edifice can enhance its selectivity.^[73] In the following example, a chiral rhodium complex could be encapsulated in a non-chiral supramolecular cage **67** via coordination-driven self-assembly

of macrocyclic dipalladium complexes and tetracarboxylate Zn-porphyrins (Scheme 25).^[74] Interestingly, rhodium complex **68** performs the regio- and enantioselective hydroformylation of styrenes with much higher chiral induction than the non-encapsulated version of the catalyst. Through spectroscopic analysis, the authors confirmed that the electronic properties of **68** and its first coordination sphere remained unchanged after encapsulation. The enhanced enantioselectivity seems to stem from a modification of the secondary coordination sphere upon the inclusion of the catalyst inside the cage. This shows that an enantioselective outcome can be obtained via an indirect through-space control of the chirality around the catalyst center.



Scheme 26. Key factors that can be considered in the design of the local environment.

Scheme 27. Adaptive and switchable catalysis – molecular control of the reaction outcome; λ = wavelength; E = applied potential.

Scheme 28. Towards a molecularly controlled catalysis and its implications for sustainable synthesis.

Prospects for Bond Activation and Catalysis

Meeting the challenges of sustainable and *Green Chemistry* correlates with the progress made in catalysis. The examples discussed have already alluded that precise molecular control

of the bond activation process could be achieved. To succeed, we believe it is necessary to consider the molecular catalyst as a system. Such a system includes a transition metal that synergistically integrates a local (e.g., ligand architecture) and a non-local (e.g., reaction conditions, renewable resources) envi-

ronment. The ligand framework serves as an immediate local environment that strongly influences the catalyst (Scheme 26). Through the anchoring parts and cooperative sites, the properties of the system can be modulated (e.g., activity, flexibility, solubility, stability, selectivity).

The ligand environment can also act as a proton or electron reservoir and thus be involved in the activation and selective transfer of various small molecules. This constitutes a step forward in the direction of an atom-economy. By undergoing one-pot multicomponent reactions, the number of steps, the usage of solvents, and chemical waste generation can be minimized. For catalysis to become successful and avoid undesired side-products, the bond formation must occur before the decomposition of transient species generated during bond activation. These species are often too unstable and decompose before transferring, adequately and selectively, the desired atom or functionality to the target molecule. In this context, a well-adapted electronic and steric environment in the metal center's vicinity can provide a unique balance between *stability* and *reactivity*. Thereby, the reactivity of these species – key to understanding the bond making and breaking reactions – can be tamed, which allows for further optimization of the catalytic cycles.

The non-local environment of a molecular system is equally important, for it supplies the necessary support to the catalyst. It can either *initiate*, *enhance*, or *shut-down* catalysis. It is often assumed that the catalyst is the main factor influencing the selectivity. However, the non-local environment (e.g., solvent, electron, and proton source, a photosensitizer (PS)) can – in some instances – overshadow the changes in catalyst architecture and more substantially contribute to the catalyst selectivity. For example, a single catalyst with a proper non-local environment can simultaneously combine several fields, leading to a high degree of sophistication. Conventionally, such protocols would require the intervention of several catalysts. Installing pH-responsive functionalities in the vicinity of the metal can also strongly influence the catalyst system. For example, it can render otherwise inactive cobalt–salen-like core active in the electrocatalytic H₂ evolution. Aside from the pH (acid-base control), other control parameters (e.g., thermal, photochemical, electrochemical, mechanochemical, coordination-driven) can produce similar effects.^[18d,68g,i,73f,75] Besides, the usage of renewable energy sources can substantially reduce the carbon footprint of the overall process.^[76] These electrons or photons produced from renewable resources can be employed to activate and modulate the molecular system's properties (e.g., changes in oxidation states of the metal, the energy of the excited- or ground-state), and hence, direct its reactivity and selectivity. Also, a supramolecular assembly, non-covalent interactions, and the orientation of external electric fields can significantly affect the catalytic system.^[77] Besides, the encapsulation of molecular catalysts into (non-local) micelles can increase the recyclability^[78] and is a step toward sustainability.^[79] Finally, taken together, all these parameters and the associated potential synergies can open the doors to adaptive and switchable catalysts that are, for instance, capable of delivering

different product platforms by varying the reaction conditions (Scheme 27).^[18e,62,80]

Conclusion

Incorporating synergistic effects into catalyst design can lead to better molecular control over the catalytic process while intertwining performance with sustainability (Scheme 28). We hope that the methods and (synergistic) effects discussed in this article will provide readers with useful insights into control parameters that have yet to be studied and applied in a sustainable molecularly controlled synergistic catalysis.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Bond Activation · Catalysis · Molecular Control · Transition Metals · Cooperativity

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