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Review

Half-Sandwich Iron Complexes: From Organometallic Reactivity to Catalyst Design

Ying Hern Tam , **Hongyu Zhong** *

School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, Singapore 637371, Singapore; YINGHERN001@e.ntu.edu.sg

* Correspondence: hongyu.zhong@ntu.edu.sg

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Abstract: Half-sandwich iron complexes have long provided a versatile platform for organometallic chemistry, yet their potential as earth-abundant catalysts with deliberately engineered reactivity is only beginning to emerge. This review examines how the reactivity of the half-sandwich framework has evolved from classical stoichiometric iron chemistry towards catalytic systems in which ligand design and ligand cooperativity play increasingly active roles. Selected studies illustrate how the iron center can encode stereochemical information, how ligand frameworks can participate directly in substrate activation and how ligand structure can redirect competing reaction pathways. These examples highlight the modularity of half-sandwich iron complexes as a platform for earth-abundant iron catalysis design and suggest broader opportunities to control their reactivity through deliberate modification of the metal–ligand environment.

Keywords: iron catalysis; ligand design; carbene; metal-centered chirality

1. Introduction

Iron is an attractive metal for sustainable catalysis owing to its abundance, low cost and low environmental impact, while its organometallic chemistry provides a versatile foundation for catalyst development.[1–4] Among the most extensively studied organoiron complexes are (η^5-C_5H_5)Fe(CO)$_2$ (Fp) and (η^5-C_5Me_5)Fe(CO)$_2$ (Fp*).[5] Their stability and accessibility made them an important platform for the study of iron–carbon bonding and reactive organoiron intermediates. The history of half-sandwich iron chemistry illustrates a recurring challenge in catalyst development: how to translate this established organometallic chemistry into controlled and productive catalysis?

The half-sandwich architecture is particularly well suited to this purpose. A strongly bound (η^5-C_5H_5) (Cp) or (η^5-C_5Me_5) (Cp*) ligand occupies one face of the metal, while a small number of ancillary ligands define the remaining coordination environment and provide sites for substrate binding and bond activation. Changes to these ligands can therefore modify the steric and electronic environment of iron without fundamentally altering the underlying metal framework. This modularity has enabled half-sandwich iron complexes to access diverse modes of catalysis, including Lewis acid catalysis, C–H functionalization, hydrogen-transfer chemistry and carbon–carbon bond formation, as comprehensively reviewed by Korb.[6]

Early studies established much of the organometallic foundation on which this chemistry rests. The Fp and Fp* platforms provided stable and accessible entry points to iron–alkyl, iron–carbene and related reactive intermediates, demonstrating that highly reactive iron–carbon species could be generated and studied within a well-defined molecular framework. Helquist and co-workers, for example, demonstrated that isolable Fp-based reagents could provide controlled access to electrophilic iron carbenes for cyclopropanation and C–H functionalization.[7] Brookhart and co-workers subsequently demonstrated that stereochemistry at the iron center could directly determine the outcome of carbene transfer, providing an early and particularly clear example of metal-centered stereochemical induction.[8] These studies established the half-sandwich framework not only as a source of reactive iron–carbon species, but also as an environment in which their reactivity and selectivity could be deliberately controlled.

The development of catalytic half-sandwich iron chemistry has since broadened considerably. Classical Fp reactivity has been incorporated into catalytic C–H functionalization and carbon–carbon bond-forming reactions, demonstrating that well-defined iron–carbon intermediates can be generated and

consumed within productive catalytic cycles.[9] More recent studies have placed increasing emphasis on the design of the ligand environment itself. Song and co-workers demonstrated how a cyclometalated *N*-heterocyclic carbene–pyridine framework can incorporate ligand participation into substrate activation,[10] while Wang and co-workers showed that modification of the ligand environment can redirect competing reaction pathways and control the regioselectivity of hydrofunctionalization.[11]

These developments point to a broader shift in the way half-sandwich iron catalysts can be designed. Early advances relied largely on identifying and exploiting the intrinsic reactivity of Fp and Fp-derived iron complexes. Increasingly, however, ligand structure is being used to determine how that reactivity is expressed: which substrates are activated, which intermediates are accessible and which competing pathways are favored. The focus therefore shifts from the intrinsic reactivity of the iron center to how the ligand environment can shape and direct that reactivity.

This review presents a selective perspective on the evolution of half-sandwich iron chemistry from organometallic reactivity toward deliberate catalyst design (Figure 1). Rather than providing a comprehensive survey of half-sandwich iron catalysis, we highlight representative works in which the structure of the metal–ligand framework provides a clear connection to reactivity or selectivity. Particular attention is given to examples in which metal-centered stereochemistry, ligand cooperativity or ligand structure directs substrate activation and reaction pathways. These studies provide a basis for considering how the modularity of half-sandwich iron complexes might be used to develop more general principles for controlling their catalytic reactivity.

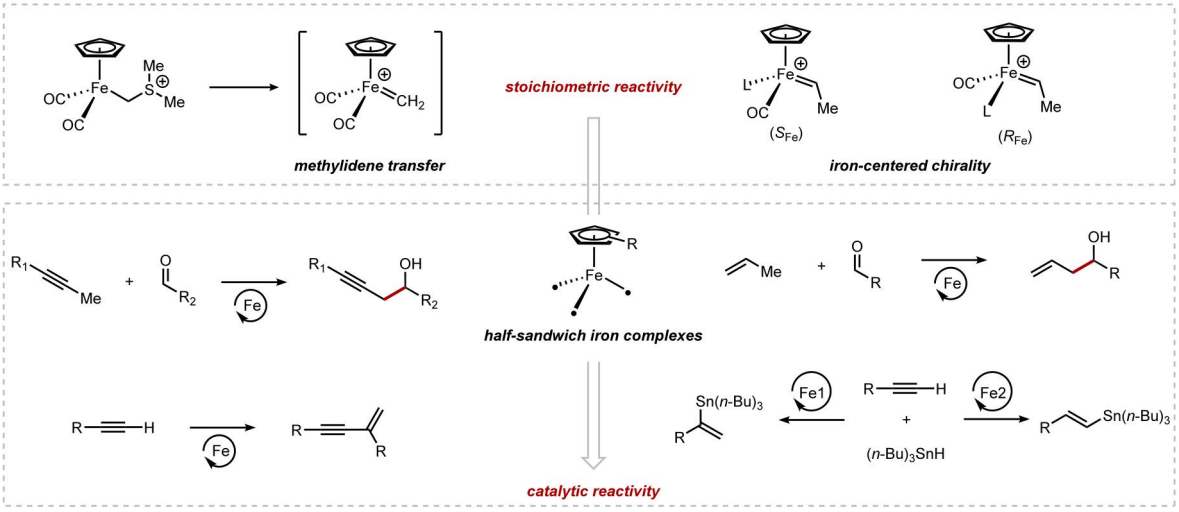

Figure 1. From stoichiometric half-sandwich organoiron chemistry to catalytic reactivity.

2. Discussion

2.1. Electrophilic Iron Carbene in Stoichiometric Cyclopropanation and C-H Insertion

The early development of half-sandwich iron chemistry established the Fp framework as a practical platform for accessing reactive iron–carbon species. An early milestone in half-sandwich iron–carbene chemistry was reported by Brookhart and Nelson, who isolated and characterized (η^5-C_5H_5)(L^1)(L^2)Fe=CHPh$^+$ (L^1, L^2=CO or L^1=CO, L^2=PPh_3) by $^1H/^{13}C$ NMR spectroscopy, establishing the half-sandwich iron framework as a viable platform for stabilizing otherwise highly reactive iron carbenes.[12] In contrast to the highly electrophilic, non-heteroatom-stabilized carbenes reported by Brookhart and Nelson, Winter and co-workers later synthesized and structurally characterized the Fischer-type carbene complex (η^5-C_5H_5)(I)(CO)Fe=C(OEt)Ph by X-ray crystallography, providing direct structural evidence for an Fe–carbene bond within the half-sandwich framework.[13] In terms of organic transformations, Helquist and co-workers were among the first to exploit this platform for the generation and synthetic application of electrophilic iron carbene with stable Fp-based precursors that could release reactive carbene equivalents under controlled conditions, providing a useful connection between well-defined organoiron complexes and highly reactive iron–carbon intermediates.[14,15]

The conceptual appeal of this chemistry is apparent in comparison with the Corey–Chaykovsky cyclopropanation. Sulfur ylides are nucleophilic carbene equivalents and are particularly effective with electron-deficient alkenes,[16] whereas the Fp-derived carbene reagents developed by Helquist possess an electrophilic carbene carbon. This change in polarity enabled cyclopropanation of electron-rich olefins and provided a complementary approach to cyclopropane synthesis. In their 1979 study, Brandt and Helquist reported a stable, crystalline iron-containing methylene-transfer reagent that underwent

Sustain. Sci. Innov. **2026**, *1*, 103379
https://doi.org/10.54963/ssi.103379

cyclopropanation with unactivated olefins, demonstrating that a reactive iron carbene could be generated from an isolable precursor (Figure 2).[14] The chemistry was subsequently developed in broader studies of iron-carbene reactivity.[7,17]

The same Fp carbene platform was then extended to intramolecular C–H insertion.[18–21] Helquist and co-workers showed that $(\eta^5\text{-}C_5H_5)(CO)_2Fe{=}CHR^+$ complexes could be generated in situ from thioether precursors by *S*-alkylation and loss of thioanisole. The resulting carbenes underwent insertion into suitably positioned C–H bonds to form substituted bicycloalkanones. The reaction was developed into a general cyclopentane-annulation method and applied to the synthesis of sterpurene and the formal synthesis of pentalenene.[21]

The stereochemical course of these insertions provided important mechanistic insights. Stereochemical probes showed high fidelity in the transfer of stereochemical information during C–H insertion, together with substantial diastereocontrol in formation of the new C–C bond.[20] Such stereochemical fidelity is difficult to reconcile with a stepwise pathway involving formation of a freely rotating carbocation, which would be expected to result in stereochemical erosion. Instead, the results support a concerted C–H insertion through a well-defined transition state.[20]

These studies illustrate the versatility of the Fp framework in accessing electrophilic iron–carbon reactivity from stable, well-defined precursors. The ability to transfer a carbene to an alkene or insert it into a C–H bond, while retaining substantial stereochemical control, also raised a broader question: to what extent could the structure and stereochemistry of the iron complex itself be used to control the outcome of these reactions? This question became particularly clear in the subsequent studies of Brookhart and co-workers.

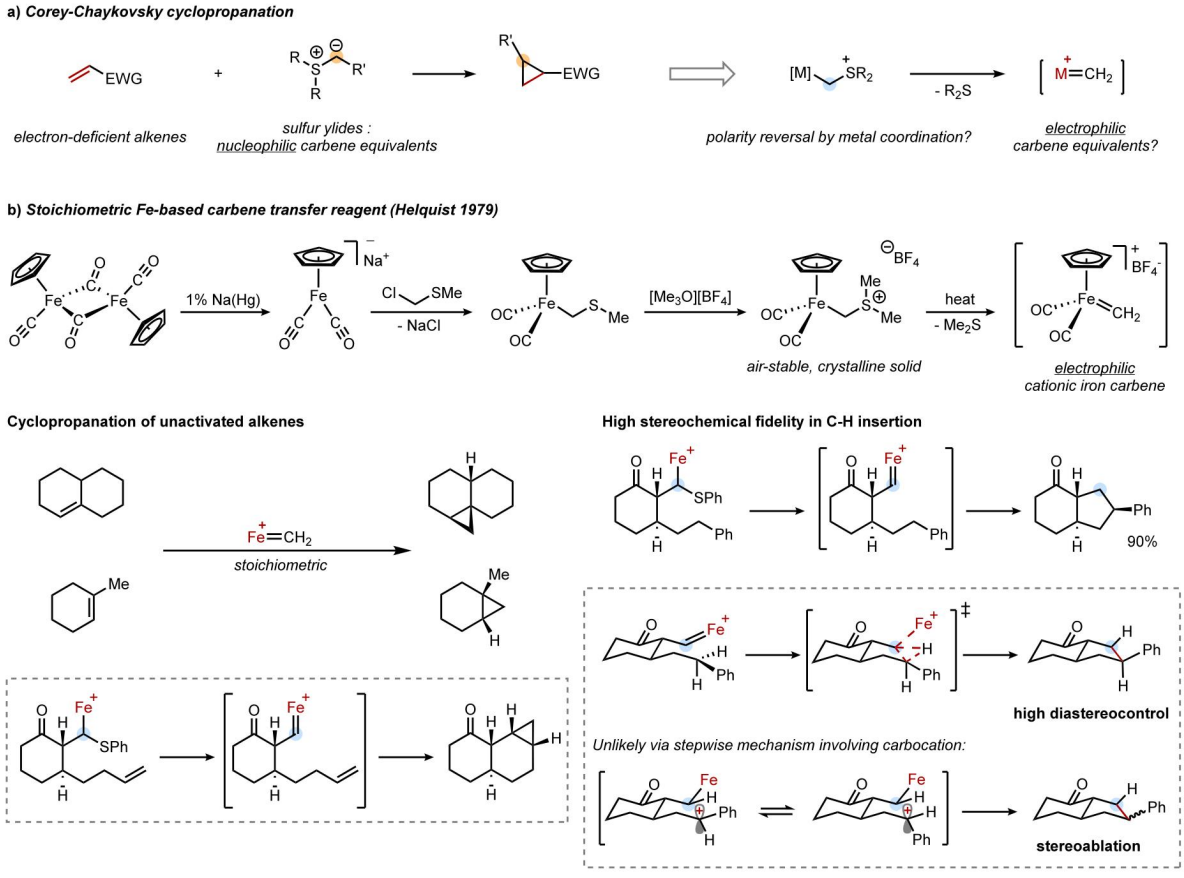

Figure 2. Electrophilic iron carbene reactivity enabled by Fp-derived reagents. Helquist's cyclopropanation and C–H insertion studies, with stereochemical probes supporting a concerted C–H insertion pathway.

2.2. Iron-Centered Chirality and Stereochemical Control of Carbene Transfer

Brookhart and co-workers provided an especially revealing demonstration that the configuration of a half-sandwich iron center can directly control the stereochemical outcome of carbene transfer. In their 1983 report, they examined the enantioselective transfer of an ethylidene ligand from chiral-at-iron complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_2R^*){=}CHCH_3^+$ to styrene (Figure 3).[22] The two diastereomeric complexes contained the same optically active phosphine but opposite configurations at iron and could be separated chromatographically. Despite this common ligand environment, the two complexes

Sustain. Sci. Innov. **2026**, *1*, 103379
https://doi.org/10.54963/ssi.103379

produced opposite cyclopropane enantiomers with similarly high optical purities, reaching approximately 84–90% *ee*. The reversal in product configuration upon stereo-inversion at iron provided compelling evidence that the stereogenic metal center, rather than the remote stereogenic element of the chiral phosphine ligand, was the dominant source of asymmetric induction.

The result was particularly striking because the stereogenic iron center was not introduced through a conventional chiral ligand pocket. Instead, chirality arose from the three-dimensional arrangement of otherwise achiral ligands around the tetrahedral iron center. The carbene ligand therefore became part of a chiral coordination environment in which the two faces available for alkene attack were rendered diastereotopic. The significance of this result was the direct link between the configuration at iron and the stereochemical outcome of an elementary organometallic reaction. The chiral environment created by the iron center differentiated the two possible modes of carbene transfer, such that reversing the configuration at iron reversed the sense of asymmetric induction.

Brookhart's 1991 study provided a more detailed picture of how this stereochemical information is expressed during carbene transfer.[23] Low-temperature NMR spectroscopy revealed that $(\eta^5\text{-}C_5H_5)Fe(CO)(PR_3)=CHCH_3^+$ complexes exist as interconverting anticlinal and synclinal isomers. The anticlinal form is thermodynamically preferred with the equilibrium strongly favoring this conformer at low temperature, while interconversion occurs with a relatively low barrier. Despite its lower population, the synclinal isomer was found to be substantially more reactive toward nucleophiles than the thermodynamically favored anticlinal isomer. Relative-reactivity and stereochemical studies therefore implicated the minor synclinal conformer as the principal reactive species in alkene attack. The subsequent bond-forming sequence was examined through stereochemical and deuterium-labelling experiments. The electrophilic carbene carbon first engages the alkene, generating a developing electrophilic center at the distal carbon of the olefin. Ring closure then occurs through electrophilic cleavage of the Fe–C bond from the opposite face, corresponding to the backside pathway proposed by the authors. Importantly, the stereochemical outcome could be rationalized without invoking free intermediates: the configuration established at the carbene carbon during the initial alkene attack is carried through the subsequent ring-closing event. The work therefore connected the observed enantioselectivity to a defined sequence of conformational selection, alkene approach and stereospecific Fe–C bond cleavage.

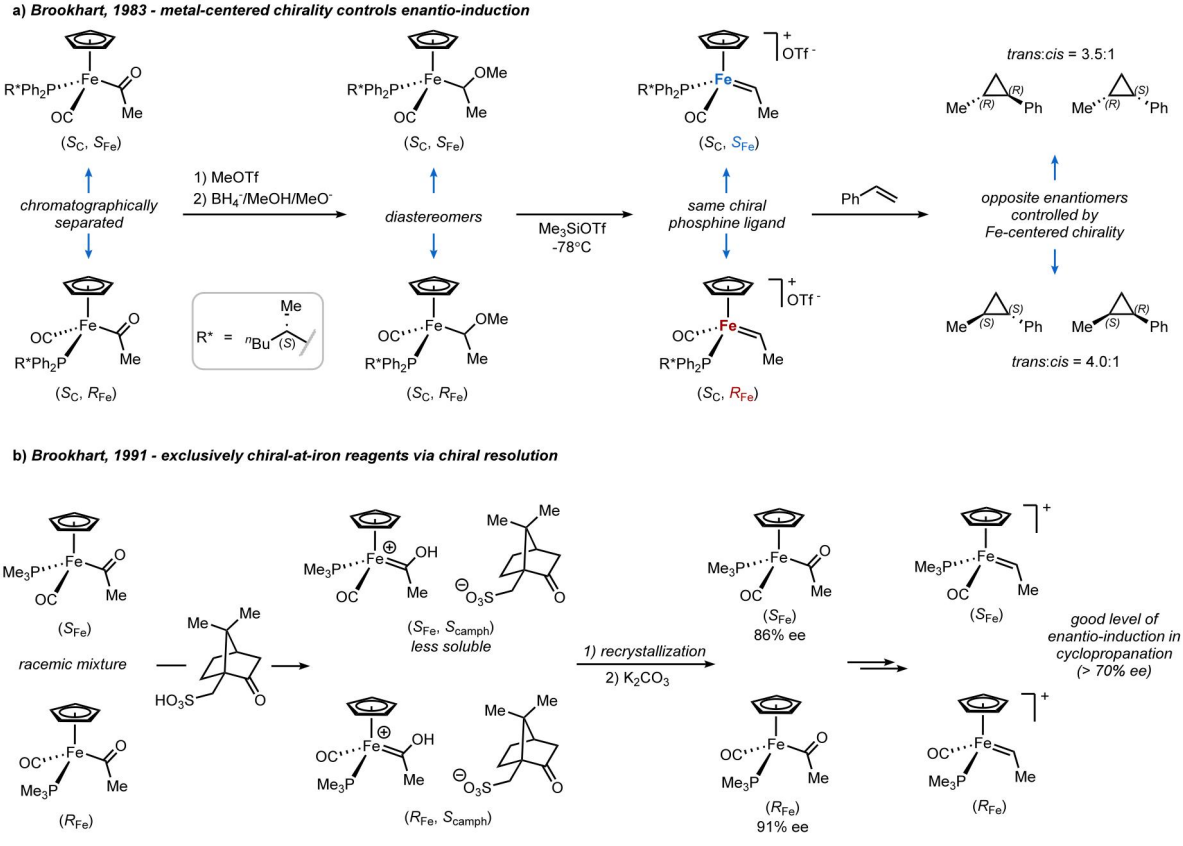

Figure 3. Metal-centered chirality and conformational control of iron carbene transfer. Brookhart's studies showed that changing the configuration at iron reverses the sense of asymmetric induction.

Sustain. Sci. Innov. **2026**, *1*, 103379
https://doi.org/10.54963/ssi.103379

The 1991 study also showed that this behavior was not restricted to the original chiral phosphine. Ethylidene complexes containing PMe_3, PEt_3, PPh_3 and the original chiral phosphine were examined, and high optical yields could be obtained with several of these ligands. In particular, the ability of small achiral phosphines to support substantial asymmetric induction emphasized that a conventional sterically elaborate chiral ligand was not required. The phosphine nevertheless influenced the relative reactivity and conformational preferences of the carbene complex, while the absolute sense of induction remained governed by the configuration at iron.

The two studies together established a direct relationship between the three-dimensional structure of a half-sandwich iron complex and the stereochemical course of its reaction. The 1983 work showed that changing only the configuration at iron could reverse the absolute configuration of the product, while the 1991 study traced this effect to the conformational and kinetic behavior of the iron carbene itself. Rather than relying solely on a chiral ligand to define the environment around an otherwise achiral metal center, these studies showed that the configuration of the iron center itself could determine the stereochemical outcome of carbene transfer. The metal-centered stereochemistry was therefore an integral part of the reactive structure, rather than simply a feature of the supporting ligand environment.

2.3. Engineering Classical Fp Reactivity for Catalysis

The development of catalytic half-sandwich iron chemistry builds on a substantial body of earlier stoichiometric work showing that Fp complexes can activate unsaturated substrates and mediate carbon–carbon bond formation. Rosenblum and co-workers demonstrated that cationic Fp–olefin complexes could undergo deprotonation to give substituted allyl–Fp complexes, with their reactivity and stereochemistry governed by the coordination environment of the metal-bound olefin.[24,25] Turo and co-workers subsequently showed that allyl–Fp complexes could react with aldehydes and other electrophiles under Lewis-acid activation, providing access to homoallylic products while retaining the iron–olefin complex prior to demetalation.[26] These studies established the underlying reactivity that later enabled the incorporation of Fp-derived iron–carbon chemistry into catalytic C–H functionalization (Figure 4).

The transition from stoichiometric Fp chemistry to catalysis is illustrated by the work of Wang and co-workers on direct propargylic and allylic C–H functionalization.[9,27,28] Their initial studies showed that cationic $(\eta^5\text{-}C_5Me_5)Fe(CO)_2$ complexes can activate otherwise unreactive C–H bonds without the need for a directing group or a strong oxidant. Coordination of an alkyne to the cationic iron center increases the acidity of the propargylic C–H bond, allowing deprotonation by a sterically hindered amine to generate a σ-allenyl iron intermediate.[9] This species then reacts with a Lewis-acid-activated aldehyde, providing a direct route to homopropargylic alcohols with high regioselectivity. Mechanistic studies were particularly informative in establishing the connection to classical half-sandwich iron chemistry. Cationic Fp*–alkyne π-complexes and neutral σ-allenyliron species could be observed or independently prepared, and their subsequent reactions with electrophiles supported their involvement in the catalytic cycle. The chemistry therefore relies on the controlled generation and subsequent reaction of well-defined iron–carbon intermediates within the catalytic cycle.

Wang and co-workers subsequently addressed a more demanding problem: applying this chemistry to simple α-olefins including propylene.[27] Rather than treating the original Fp* framework as a fixed catalyst, they modified the Cp environment of the cationic iron complexes, incorporating a fused cyclooctano framework and electron-rich arene substituents. These changes improved catalytic efficiency and selectivity and enabled allylic C–H functionalization of propylene with a broad range of aldehydes and related electrophiles. This study also showed how ligand modification can influence not only the activity of the catalyst but the selectivity of the C–C bond-forming step. Mechanistic and computational studies implicated interactions between the modified Cp ligand and the aldehyde, together with a hydrogen-bonding interaction involving the BF_3-activated electrophile, in controlling the stereochemical outcome. The ligand environment thus becomes an active element in organizing the transition state rather than simply supporting the iron center.

The tunability of the half-sandwich iron platform was further exploited by Wang and co-workers for the regioselective C(sp^2)–H functionalization of simple monosubstituted allenes.[29,30] The modified cationic Fp system selectively functionalizes the sterically less accessible internal allenic C–H bond, providing 1,1-disubstituted allenes with high contrasteric regioselectivity. Catalyst development proved central to this unusual selectivity: replacing Cp* with bulkier, more electron-rich Et_5Cp and Pr_5Cp ligands facilitated equilibration of the cationic iron–allene complexes and substantially improved catalytic efficiency. The resulting platform enabled coupling with iminium electrophiles and was subsequently extended to aldehydes through complementary control of the reaction environment using silyl triflates and $LiNTf_2$, while retaining the characteristic formation of 1,1-disubstituted allenes as a single regioisomer. Together, these studies illustrate how modification of both the Cp ligand and secondary coordination environment can tune the dynamics and reactivity of substrate-bound half-sandwich iron intermediates to access otherwise disfavored regioselectivity.

The versatility of this cationic Fp platform was further demonstrated by Wang and co-workers, who expanded its reactivity through the use of diverse electrophiles,[31–33] as well as coupling with nucleophiles through an umpolung strat-

Sustain. Sci. Innov. **2026**, *1*, 103379
https://doi.org/10.54963/ssi.103379

egy.[34] These studies illustrate how the Fp framework can evolve from a source of well-defined iron–carbon reactivity into a tunable catalytic platform: first by embedding classical iron–carbon bond formation within a C–H functionalization cycle, and subsequently by modifying the Cp environment to control catalytic efficiency and selectivity.

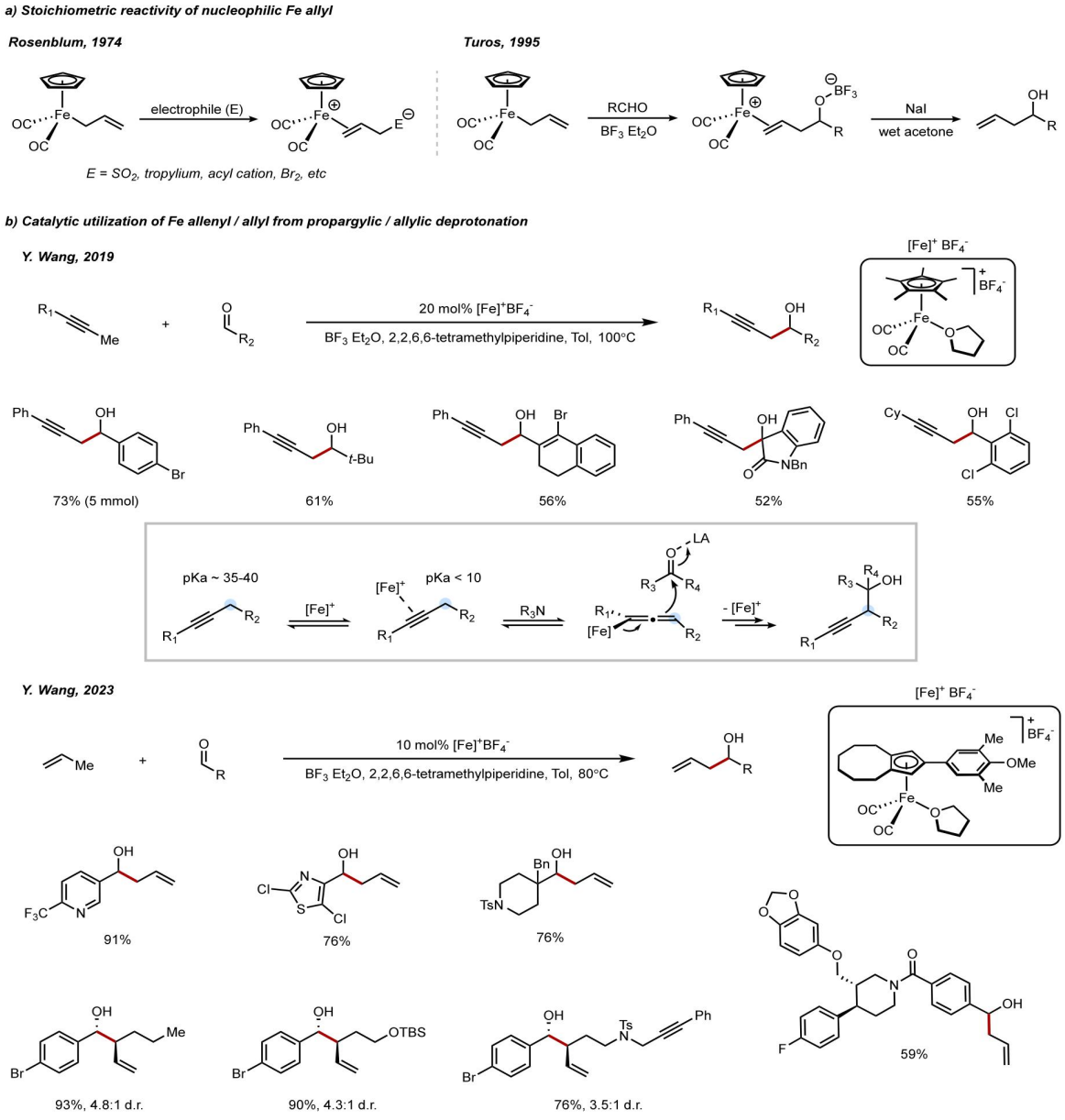

Figure 4. From stoichiometric Fp reactivity to catalytic C–H functionalization. Rosenblum and Turo established Fp-mediated olefin and allyl–iron reactivity, which Wang and co-workers developed into catalytic propargylic and allylic C–H functionalization.

2.4. Ligand Cooperativity

The role of metal-ligand cooperativity becomes more pronounced in the work of Song and co-workers on iron-catalyzed terminal-alkyne dimerization. They developed a well-defined piano-stool iron(II) complex bearing an η^5-C_5Me_5 ligand and a cyclometalated picolyl *N*-heterocyclic carbene ligand (Figure 5). The catalyst promotes highly selective geminal dimerization of terminal alkynes, providing 1,3-enynes without the competing head-to-head *E*/*Z* isomers commonly associated with alkyne dimerization.[10,35] The system also enables cross-dimerization of propargyl alcohols with aryl alkynes with high selectivity over the corresponding aryl-alkyne homodimers.

The ligand architecture is central to this reactivity. Cyclometalation converts the ancillary ligand from a conventional donor into a framework containing a covalent Fe–C bond, while the picolyl group provides an additional donor site within the same ligand environment. This arrangement creates a well-

Sustain. Sci. Innov. **2026**, *1*, 103379
https://doi.org/10.54963/ssi.103379

defined coordination sphere around iron and places the metalated carbon in close proximity to substrates bound at the metal. Stoichiometric studies, isotope effects, identification of iron-containing intermediates and computational analysis support a mechanism involving alkyne coordination and C–H activation followed by migratory insertion.[10]

The resulting selectivity is notable because terminal-alkyne dimerization presents several possible C–C bond-forming pathways and can readily generate mixtures of regio- and stereoisomers. In the Song system, the catalyst architecture instead favors formation of the geminal 1,3-enyne across a broad range of aryl and aliphatic alkynes, as well as substrates containing propargylic alcohol and amine functionality. The successful cross-dimerization of propargyl alcohol with aryl alkynes further demonstrates that the ligand environment can discriminate between competing coupling pathways rather than simply promote alkyne activation. In their subsequent works, Song and co-workers have continued to improve the efficiency of alkyne dimerization through ligand design,[36,37] while simultaneously expanding the reactivity of ligand-cooperative piano-stool iron(II) complexes toward new transformations.[38,39]

The Song system thus illustrates a different aspect of ligand-controlled reactivity in half-sandwich iron chemistry: the ligand framework is constructed to create a defined reactive environment in which substrate activation and subsequent bond formation can be selectively orchestrated. Cyclometalation is not merely a means of fixing the ligand geometry or increasing its donor strength; it forms part of the organometallic structure through which the catalyst engages the alkyne. This provides a useful example of how deliberate ligand architecture can convert the intrinsic reactivity of an iron center into controlled catalytic selectivity.

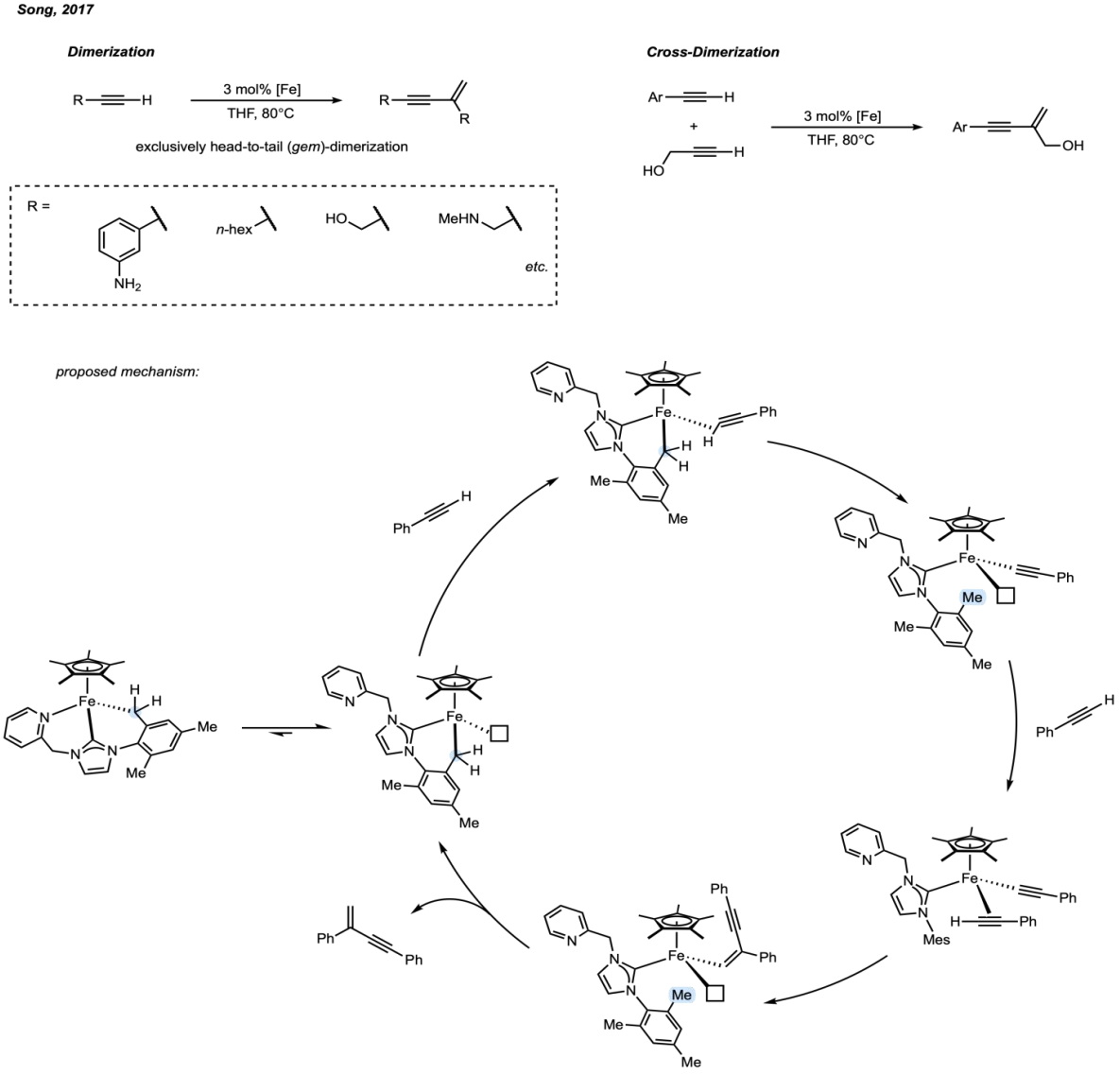

Figure 5. Ligand cooperativity in iron-catalyzed alkyne dimerization. Song and co-workers' cyclometalated NHC–pyridine iron complex enables selective geminal dimerization of terminal alkynes through cooperative ligand participation.

Sustain. Sci. Innov. **2026**, *1*, 103379
https://doi.org/10.54963/ssi.103379

2.5. Ligand-Controlled Divergent Reactivity

Wang and co-workers have shown that ligand design can determine which elementary step initiates catalysis in closely related half-sandwich iron complexes (Figure 6).[11] Their study of alkyne hydrostannation provides a particularly clear example: changing the X-type ligand from amido to aryloxide switches the reaction between Markovnikov and anti-Markovnikov hydrostannation. The two catalysts therefore give different regioisomers from the same iron platform by engaging the reactants through distinct activation pathways.[11]

The mechanistic origin of this divergence lies in the reactivity of the ionic Fe–X bond. With the amido complex, activation of nBu$_3$SnH generates an iron hydride species, followed by *syn*-addition of the Sn–H unit across the alkyne to give the branched α-vinylstannane. In contrast, the aryloxide complex promotes activation of the terminal C(sp)–H bond of the alkyne, generating an iron–vinylidene intermediate. Subsequent addition of the Sn–H unit through a *gem*-addition pathway gives the complementary β-vinylstannane. Deuterium-labelling and kinetic studies provided evidence for these distinct reaction sequences and their different turnover-limiting steps.

The striking feature is therefore not simply that the ligand changes regioselectivity, but that it determines which reactant is activated first. Modification of a single ligand site changes the nature of the reactive iron species and, consequently, the sequence of elementary steps leading to product formation. The ligand environment thus acts as a means of selecting between competing catalytic pathways rather than merely tuning the reactivity of a common intermediate.

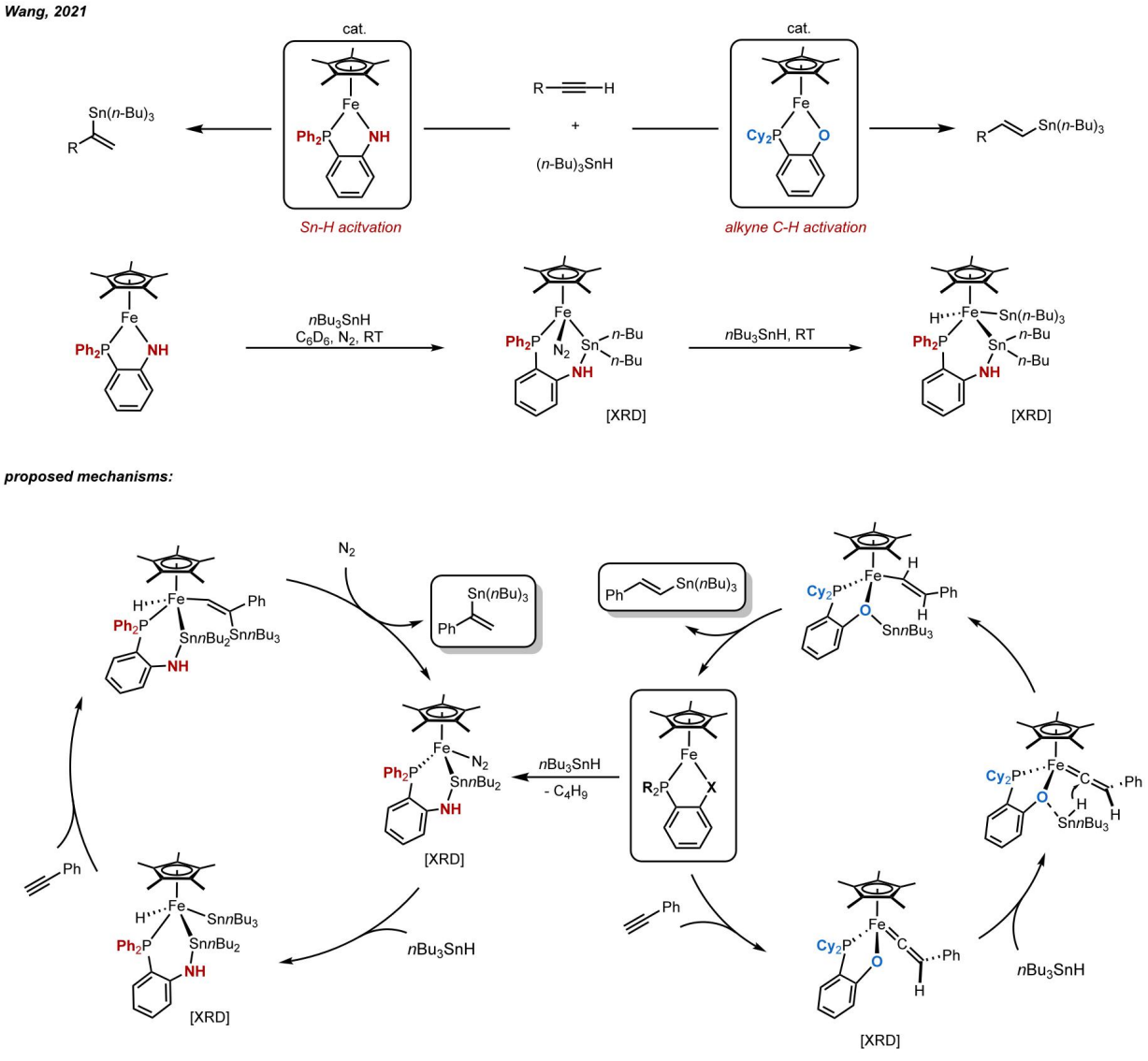

Figure 6. Ligand-controlled divergent reactivity in iron-catalyzed hydrostannation. Wenguang Wang and co-workers use ligand-dependent activation of Sn–H or C(sp)–H bonds to control the regioselectivity of alkyne hydrostannation.

Sustain. Sci. Innov. **2026**, *1*, 103379
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This example illustrates a particularly powerful aspect of ligand design in half-sandwich iron catalysis. By controlling the polarity and reactivity of the Fe–X bond, the ligand can dictate the entry point into the catalytic cycle and thereby program the reaction pathway and product selectivity. Such control is especially valuable for iron, where closely related organometallic species can often support substantially different reaction mechanisms. The ligand is therefore not simply a spectator or a stabilizing element of the catalyst, and its identity can determine the mechanistic route through which the catalyst operates. Wang and co-workers have also extended the reactivity of half-sandwich iron–amido complexes to small-molecule activation, exploiting metal–ligand cooperativity to enable transformations including ammonia oxidation, CO_2 hydroboration and alkene isomerization–reductive deuteration. These studies highlight the potential of the half-sandwich framework for feedstock valorization and relevance to sustainable catalysis.[40–42] Please see Table 1 for a summary of representative work discussed.

Table 1. Summary of representative works discussed.

Representative System	Ligand/Catalyst Design	Transformation	Activation Mode/Key Intermediate	Selectivity	Representative Conditions	Scope/Limitations
Helquist	Cationic Fp (η^5-C_5H_5)$Fe(CO)_2^+$	Carbene transfer	Electrophilic Fe-methylidene	Unactivated alkenes, labile C-H bonds	Stoichiometric	Mechanistic precedent, not catalytic
Brookhart	Chiral-at-Fe (η^5-C_5H_5)$Fe(CO)(PR_3)$	Carbene transfer	Electrophilic Fe-ethylidene; reactive synclinal conformer	75–95% optical yield; Fe configuration controls product	Stoichiometric	Mechanistic precedent, not catalytic
Y.-M. Wang	Fp*/modified Cp dicarbonyl	Allylic/propargylic C-H functionalization	π-coordination → deprotonation → Fe-C intermediate	High regio-/di-astereoselectivity	10–20 mol% [Fe], $BF_3{\cdot}Et_2O$, TMPH, 80–100 °C	Internal olefins less selective
Song	Cp*Fe cyclometalated NHC-pyridine	Terminal-alkyne dimerization	Cooperative C-H activation/Fe-acetylide formation	*Gem*-selective	1–3 mol% [Fe], THF, 80 °C	Bulky/ester alkynes limited
W. Wang	Fe-amido vs. Fe-aryloxide	Alkyne hydrostannation	Sn-H activation vs. C(sp)-H activation	α vs. β regioselectivity	2 mol% [Fe], toluene, RT	Catalyst-dependent scope

3. Conclusion

The development of half-sandwich iron chemistry illustrates how an established organometallic framework can evolve from a platform for stoichiometric reactivity into an emerging catalyst platform. The examples discussed here show several ways in which the reactivity of this framework can be controlled. Brookhart's studies established metal-centred chirality as a source of stereochemical control, while subsequent work demonstrated that ligand structure can participate directly in substrate activation, influence the course of elementary steps, or redirect competing reaction pathways. At the same time, catalytic adaptations of classical Fp chemistry have shown that well-defined iron–carbon reactivity can be incorporated into productive catalytic cycles.

These studies point to an opportunity to move beyond the discovery of individual reactions toward more general approaches to catalyst design. The modularity of half-sandwich complexes makes the ligand environment an unusually accessible design variable: modification of the Cp or Cp* ligand, ancillary donors, or the stereochemical environment at iron can alter coordination, substrate activation and the relative accessibility of competing pathways while preserving the underlying half-sandwich architecture. Developing a more predictive understanding of these relationships will be important for reducing the reliance on empirical catalyst optimization. These design principles may also provide opportunities for feedstock valorization. The functionalization of simple alkenes, alkynes and allenes demonstrated across the representative works suggests how half-sandwich iron complexes can transform relatively simple unsaturated building blocks into more structurally and functionally complex products, as exemplified by the direct use of propylene in C(sp^3)-H hydroxyalkylation.

An especially promising direction lies beyond the predominantly two-electron chemistry represented in the examples discussed here. Iron can support ligand-centered redox chemistry and one-electron pathways, yet these features remain largely unexplored within half-sandwich catalyst design. Redox-non-innocent ligands could provide new ways to store and transfer electrons within the catalyst, while controlled access to radical intermediates could open reaction pathways that are difficult to achieve through conventional two-electron mechanisms. An important challenge will be to incorporate these features without sacrificing the structural and stereochemical control that makes half-sandwich complexes attractive as catalyst platforms.

More broadly, the next stage of development may lie in combining these different modes of control within a single molecular framework. Metal-centered chirality, ligand cooperativity, ligand redox non-innocence and control over one- versus two-electron reactivity need not be viewed as separate design strategies. Their deliberate integration could provide new ways to program the structure, electronic state and reactivity of transient iron intermediates. Such an approach would shift half-sandwich iron chemistry from adapting established organometallic reactivity toward deliberately engineering the

Sustain. Sci. Innov. **2026**, *1*, 103379
https://doi.org/10.54963/ssi.103379

metal–ligand environment to determine how the catalyst reacts.

Half-sandwich iron complexes therefore offer more than a well-established collection of organometallic motifs. Their modular architecture provides a platform in which the metal, ligand and their interactions can be treated as interconnected design variables. Establishing general relationships between these molecular features and catalytic function could help turn the considerable reactivity of half-sandwich iron complexes into a more predictable platform for selective and sustainable catalysis.

Author Contributions

Writing—original draft preparation, H.Z. and Y.H.T.; writing—review and editing, H.Z. and Y.H.T.; supervision, H.Z.; All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflicts of interest.

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