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Catalytic Activity of Iron N-Heterocyclic Carbene Complexes

Badri Nath Jha, Nishant Singh and Abhinav Raghuvanshi

Abstract

Recent research towards development of more efficient as well as cost effective catalyst as a substitute to traditional precious metal catalysts has witnessed significant growth and interest. Importance has been given to catalyst based on 3d-transition metals, especially iron because of the broad availability and environmental compatibility which allows its use in various environmentally friendly catalytic processes. N-Heterocyclic carbene (NHC) ligands have garnered significant attention because of their unique steric and electronic properties which provide substantial scope and potential in organometallic chemistry, catalysis and materials sciences. In the context of catalytic applications, iron-NHC complexes have gained increasing interest in the past two decades and could successfully be applied as catalysts in various homogeneous reactions including C–C couplings (including biaryl cross-coupling, alkyl-alkyl cross-coupling, alkyl-aryl cross-coupling), reductions and oxidations. In addition to this, iron-NHC complexes have shown the ability to facilitate a variety of reactions including C-heteroatom bond formation reactions, hydrogenation and transfer-hydrogenation reactions, polymerization reactions, etc. In this chapter, we will discuss briefly recent advancements in the catalytic activity of iron-NHC complexes including mono-NHC, bis-NHC (bidentate), tripodal NHC and tetrapodal NHC ligands. We have chosen iron-NHC complexes because of the plethora of publications available, increasing significance, being more readily available, non-toxic and economical.

Keywords: N-heterocyclic carbene (NHC), singlet carbenes, triplet carbenes, percent buried volume ($\% V_{\text{bur}}$), σ -donation, π -donation, CO complexes, NO complexes, halide complexes, donor-substituted NHCs, pincer motifs, scorpionato motifs, macrocyclic ligands, piano stool motifs, iron-sulfur clusters, C-C bond formations, allylic alkylations, C-X (heteroatom) bond formations, reduction reactions, cyclization reactions, polymerization

1. Introduction

Story of N-heterocyclic carbene builds up from an unstable non-isolable reactive species to a stable and highly flourished ligand for the synthesis of a variety of organometallic compounds and many important catalytic reactions. Based on the orbital occupancy of the electrons, carbenes can be classified as singlet and triplet carbenes. In singlet carbene, a lone pair of electron occupies sp^2 -hybrid orbital (**Figure 1A**)

whereas, in triplet carbene, two single electrons occupy two different p-orbitals (**Figure 1B**). Carbenes are inherently unstable, hence highly reactive species due to incomplete electron octet. Initial reports of isolable carbene came in the late 1980s, where the carbene is stabilized by adjacent silicon and phosphorus substituents.

Credit for the discovery of stable and isolable carbene goes to Arduengo, where carbene carbon is a part of a nitrogen heterocycle and gave the first N-heterocyclic carbene (NHC) compound called 1,3-di(adamantyl)imidazol-2-ylidene briefly called IAd (**Figure 2A**) [1]. Since then NHC compounds are enjoying their success to several dimensions of synthesis and organic transformations.

1.1 Structure and general properties of NHCs

Thus, a heterocyclic compound with a carbene carbon and at least a nitrogen atom adjacent to it within the ring can be termed as NHC [2]. NHCs are singlet carbenes and their remarkable stability is contributed by both steric and electronic effects. Dimerization of carbene carbon is kinetically frustrated by keeping bulky groups on the two sides of the carbene carbon, as is the case with IAd (**Figure 2A**) where two adamantyl groups are attached to the nitrogen atoms (adjacent to the carbene center). Nolan and his co-workers have quantified the steric properties in terms of the 'buried volume' parameter ($\% V_{bur}$) (**Figure 2B**) [3]. Metal ion of the NHC-metal complex is assumed to be at the center of a sphere and then $\% V_{bur}$ is calculated as the portion of the sphere occupied by the NHC ligand (**Figure 2B**). Larger the value of $\% V_{bur}$, greater is the steric repulsion at the metal center. The buried volume is usually determined from crystallographic data of the NHC-metal complex [4] or directly from theoretical calculations with the free NHC.

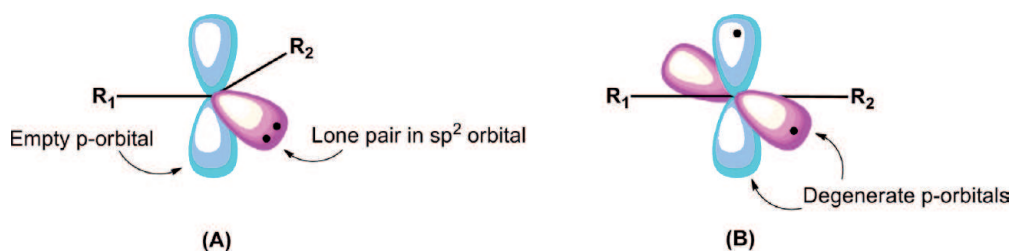


Figure 1.
(A) Singlet carbenes; (B) triplet carbenes.

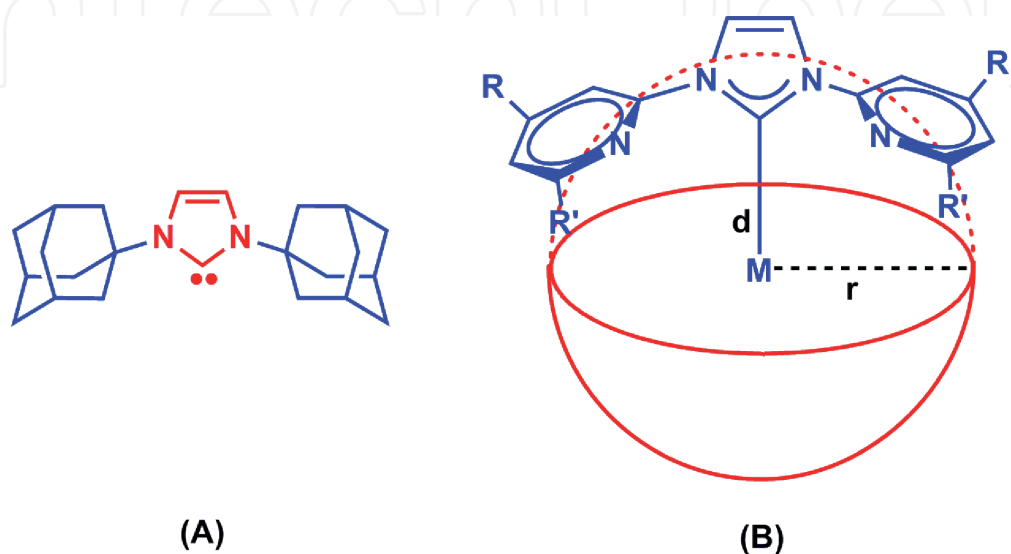


Figure 2.
(A) Structure of IAd; (B) percent buried volume ($\% V_{bur}$).

The value of % V_{bur} is affected by both the nature of the NHC ligand as well as the geometry of the NHC-metal complex; therefore, data is useful only for the comparison within the same family of complexes. A small change in the structure of ligands may bring more than 10% increase or decrease in percent buried volume [5]. Caution should also be paid as the calculation of % V_{bur} is carried out in solid-phase through crystallographic data analysis or in gas phase by DFT calculation. In both the methods the behavior of the complexes in solution and solvation is not considered where ligand may adopt several conformations. The stability of an NHC is far more affected by the electronic factor. Carbene carbon of NHC has three sp^2 -orbitals orientated in triangular planar fashion and one p_z -orbital perpendicular to the plane of the NHC ring. Two sp^2 -orbitals are bonded with two nitrogen atoms in the ring and one sp^2 -orbital houses the lone pair of electrons. The two nitrogen atoms stabilize the carbene carbon in two ways: (i) by withdrawing the sigma-electrons through inductive effect and (ii) through a π -electron donation to the empty p_z -orbital of the carbene carbon (meso-meric effect). This π -electron donation is so strong that NHCs are also described by its zwitterionic resonance structure and is evident by the intermediate bond length of carbene C-N bond (1.37 Å) in IAd, which falls in between C-N single bond length (1.49 Å) and C-N double bond length (1.33 Å) of the corresponding analog compounds (IAdH₂ and IAdH⁺ respectively). In the molecular orbital model, sp^2 and p_z -orbital can be described as HOMO (A_1 non-bonding molecular orbital) and LUMO (B_2^* bonding molecular orbital), respectively (**Figure 3**) [6, 7]. The cyclic nature of NHCs is also an important structural aspect as it creates a preferable situation for the singlet state by forcing the carbene carbon to adopt a more sp^2 -like arrangement.

Like the phosphines, the electron-donating capability of NHCs is evaluated using Tolman electronic parameter (TEP) [8]. Any build-up of electron density on the metal center of the complex [Ni(CO)₃(NHC)] due to electron donation by the NHC is reflected by the decrease in the infrared-stretching frequency of CO bonded with the metal ion. Now-a-days, instead of [Ni(CO)₃(NHC)], less toxic [(NHC)IrCl(CO)₂] and [(NHC)RhCl(CO)₂] are used and a correlation formula is used [Eqs. (1) and (2)], respectively [9, 10].

$$TEP = 0.847 \cdot \nu_{CO}(\text{Ir}) + 336 \text{ cm}^{-1} \quad (1)$$

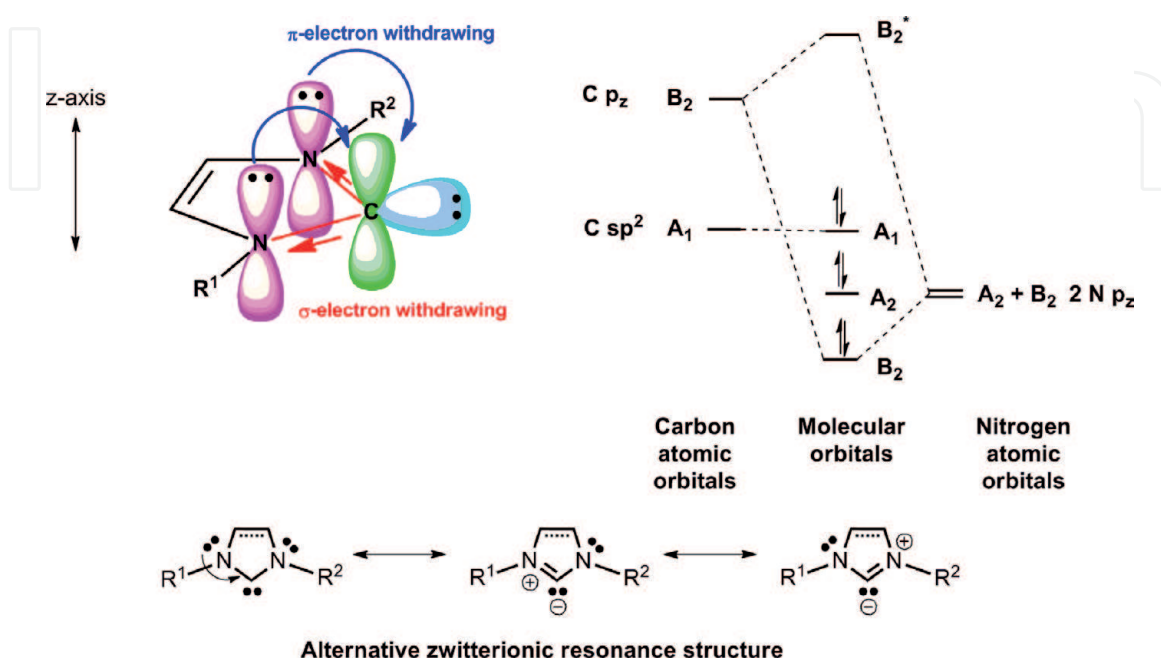


Figure 3.
Molecular orbital diagram of an NHC.

where, $\nu_{\text{CO}}(\text{Ir})$ = average IR-stretching frequency of CO in $[(\text{NHC})\text{IrCl}(\text{CO})_2]$ complex.

$$\nu_{\text{CO}}(\text{Ir}) = 0.8695 \cdot \nu_{\text{CO}}(\text{Rh}) + 250.7 \text{ cm}^{-1} \quad (2)$$

where, $\nu_{\text{CO}}(\text{Ir})$ = average IR-stretching frequency of CO in $[(\text{NHC})\text{IrCl}(\text{CO})_2]$ complex, and $\nu_{\text{CO}}(\text{Rh})$ = average IR-stretching frequency of CO in $[(\text{NHC})\text{RhCl}(\text{CO})_2]$ complex.

1.2 Synthesis of NHCs precursor and generation of carbene

Azolium or dihydroimidazolium salts are sufficiently stable solids and the generation of NHCs can be carried out *in situ* by their deprotonation using non-nucleophilic bases such as sodium hydride, butyllithium or *t*-butoxide. Alkoxides form an adduct with azolium salt, however, in presence of transition metal precursor, NHC is transferred to the metal and usually moves toward complex formation rather than the disruption of the azolium ring. Generation of NHCs is also carried out using mild metal oxides like silver (I) or copper (I) oxides where after generation, NHC forms NHC-silver(I) or copper(I) complexes and *in situ* transfer of NHC occurs to the desired metal center. A general protocol for the synthesis of NHCs and NHC precursor **11** is outlined below in **Figures 4** and **5**, respectively [11, 12].

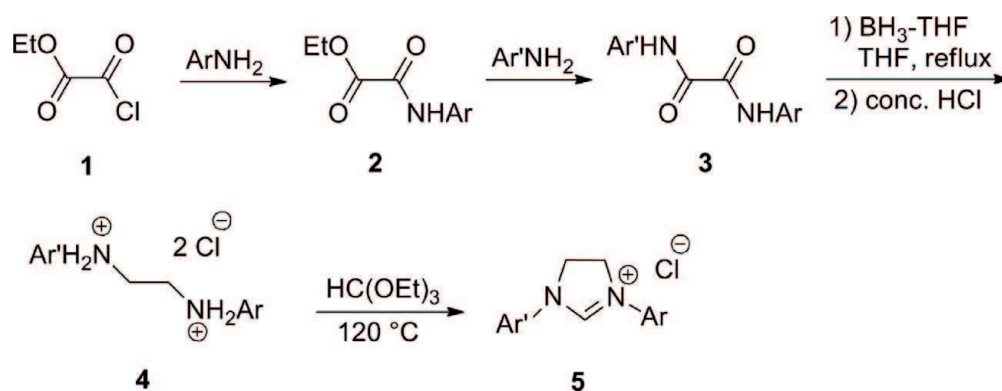


Figure 4.
General protocol for the synthesis of unsymmetrical substituted NHCs.

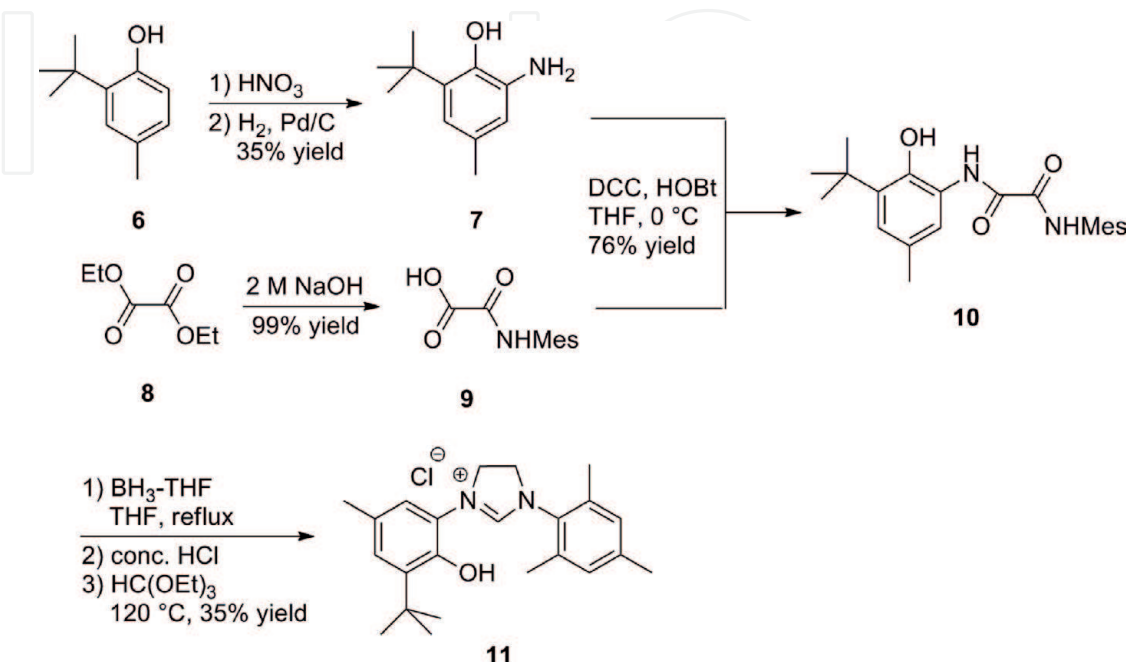


Figure 5.
Synthesis of NHC precursor **11**.

1.3 Generation of NHCs

Formation of saturated and unsaturated NHCs upon treatment with an alkoxide base is shown in **Figure 6A** and **B**, respectively [13].

1.4 Coordination of NHCs to transition metals

Thus, the coordination of NHC ligand to the transition metal ion occurs largely through the *strong σ -donation* of the formal sp^2 -hybridized lone pair to a σ -accepting orbital of the transition metal and a *weak but not inconsiderable π -donation* [14] either in the form of π -back donation from metal to the p_z orbital of the ligand or vice versa [15, 16]. However, in practice a single bond is drawn since the free rotation energy across the M-C bond is very low (**Figures 2B** and **6**).

1.5 Phosphine versus NHCs

NHCs are being compared with strong sigma donating ligands like phosphines and cyclopentadienes. As a ligand, NHCs edge ahead of phosphines on several points:

- i. *Electron donor*: NHCs are relatively stronger electron-donor than phosphines and produce thermodynamically stronger metal-ligand bonds, except when there are steric constraints interfere with metal-ligand binding [17].
- ii. *Steric properties*: Whereas the spatial arrangement of steric bulk takes up a *cone-shape* due to sp^3 -hybridization of phosphines; most of the NHCs results in *umbrella-shaped* steric bulk and the orientation of the substituent on the two nitrogen atoms are more toward the metal center. Thus, the steric crowd around the metal center can be tuned by changing the substituent on the two nitrogen atoms and the heterocyclic ring, if required.
- iii. *Ease of varying their steric and electronic properties*: There are several well-established synthetic routes to tune the steric and electronic properties of NHCs, whereas it is usually difficult to tune the properties to the desired level for the phosphines.

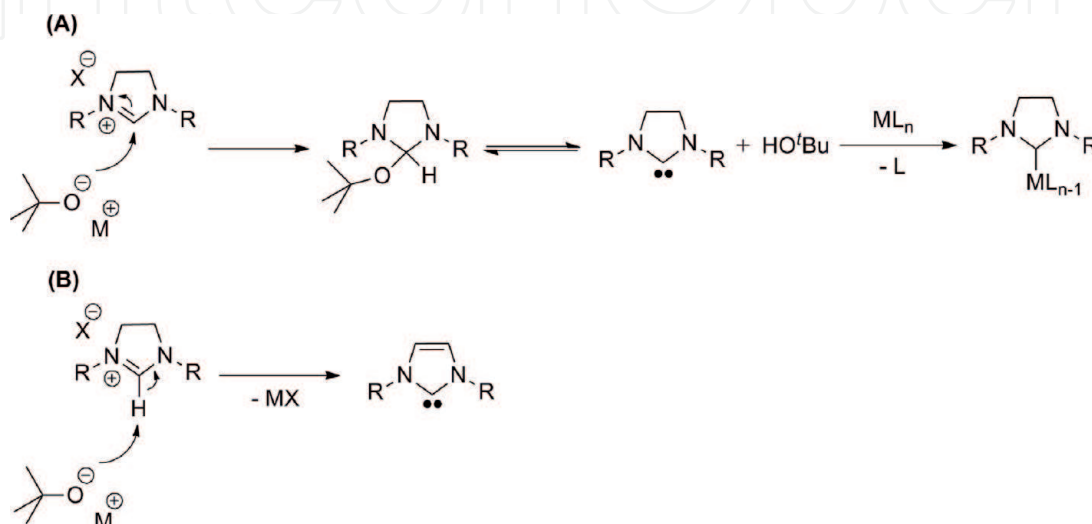


Figure 6.
 Treatment with an alkoxide base leads to formation of (A) saturated NHCs; and (B) unsaturated NHCs.

- iv. In the case of phosphines, changing the substituent on the phosphorus inevitably changes both steric and the electronic properties whereas each parameter can be modified independently through modifying the substituents on nitrogen, functionalities on the heterocycle and the type of heterocycle itself.

2. Various motifs of Fe-NHC complexes

The structural diversity in various motifs of Fe-NHC complexes is shown in **Figure 7** and each of them is explained below along with their known applications in different areas.

2.1 Mono- and bis-(mono- or chelating) carbene ligands

2.1.1 CO complexes

The chemistry of Fe-NHC complexes began with the synthesis of their unsaturated and saturated ligand precursors with carbonyl as their motifs, and extensive studies on molecular structure determination and reactivity (**Figure 8A–D**). These CO complexes were further subjected to substitution reaction, e.g. ligand exchange with monophosphines and oxidation, to develop newer Fe-NHC complexes (on oxidation their geometry tends to change from trigonal bipyramidal to distorted square pyramidal). These transformations, in progression, led to the formation of new classes of complexes with novel attributes viz. monocarbene, bis-monocarbene, and chelating biscarbene ligands having variable oxidation states of iron from Fe(0) to Fe(II), which contributed to new horizons in bioinorganic chemistry and biomimetic systems e.g. Novel Fe(II) monocarbene complexes (**Figure 8C**) as models for basic structure of the monoiron hydrogenase [18].

2.1.2 NO complexes

Synthesis of novel and intriguing Fe-NHC complexes in the field of biomimetic chemistry e.g. dinitrosyliron complexes (DNICs) (**Figure 8G**) displaying a variety of vital biological functions [18], forced the scientific community to shift their attention toward novel monocarbene and bis-monocarbene ligands having nitrosyl as their structural attributes (**Figure 8E–G**). Not only as biomimetic structural models, these nitrosyl complexes can act as catalyst in chemical transformations e.g. allylic alkylation [18, 19].

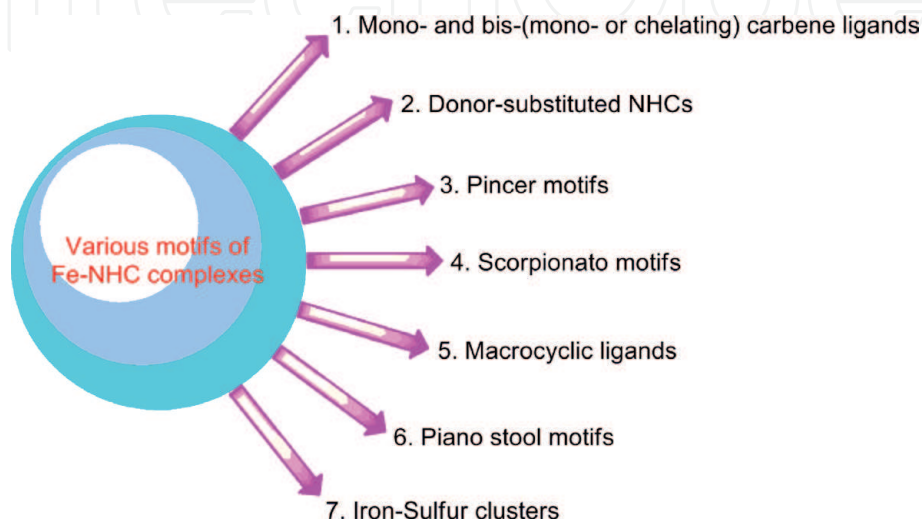


Figure 7.
Different motifs of Fe-NHC complexes.

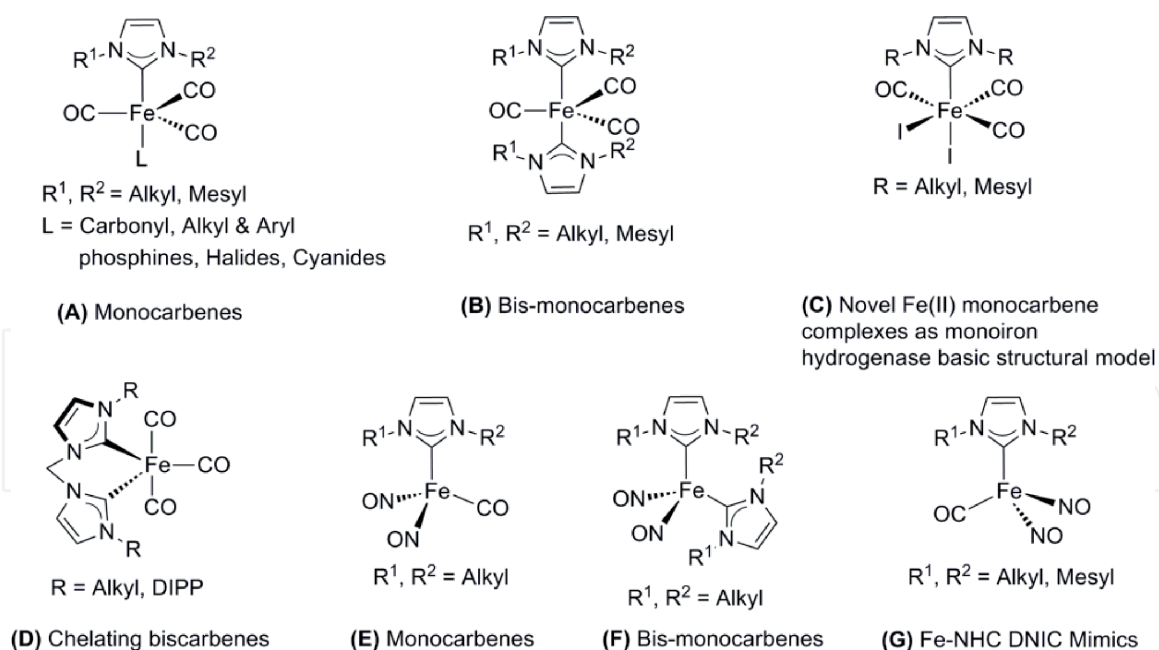


Figure 8.
(A–D) CO complexes; (E–G) NO complexes.

2.1.3 Halide complexes

Just like carbonyl and nitrosyl motifs in Fe-NHCs chemistry, halides do play a major role in influencing the role of Fe-NHC complexes in both catalysis as well as biomimetics. Halide complexes catalytic role varies from polymerization catalysis by bis-monocarbene dihalide Fe-NHC complexes [18, 20] C-C cross-coupling reactions catalyzed by dinuclear Fe-NHC imido complexes [18, 21] to catalytic hydrosilylation by ethylenediamine-derived Fe-NHC complex [18]. Depending upon the structural versatility in halide complexes, many subclasses have been synthesized and studied, namely monocarbene ligands, bis-monocarbene ligands, chelating biscarbene ligands, dinuclear Fe-NHC imido complexes, halide-bridged Fe-NHC complexes, immobilized Fe-NHC complexes, three-coordinate Fe-NHC complexes (**Figure 9A–G**).

2.2 Donor-substituted NHCs

Effects on the reactivity of organometallic iron complexes could be observed when the ligand environment changes from CO, NO, halides to donor-substituted NHC ligands (**Figure 10A**). These donor-substituted NHC ligands possess nitrogen or oxygen as heteroatoms, thus present themselves as potential coordinating “arms” attached to the NHCs and exhibit coordination from bi- to pentadentate as ligand systems. These complexes have shown their catalytic role in ring-opening polymerization of ϵ -caprolactone [18, 22].

2.3 Pincer motifs

Chelating biscarbene pincer ligands (**Figure 10B**) are an extension of donor-substituted NHCs in Fe-NHC chemistry, where instead of the presence of heteroatoms as “arms”, two NHC units are linked by a pyridyl moiety and hence “chelation”. Structurally, pincer motifs exhibit two coordination geometries predominantly, octahedral and square pyramidal, due to their strict binding mode to three adjacent coplanar centers. Catalysis by Fe-NHC complexes bearing pincer motifs has been demonstrated by their catalytic role in concerted C-H oxidation addition reaction [18], hydroboration reaction [18, 23], and hydrogenation reaction [18].

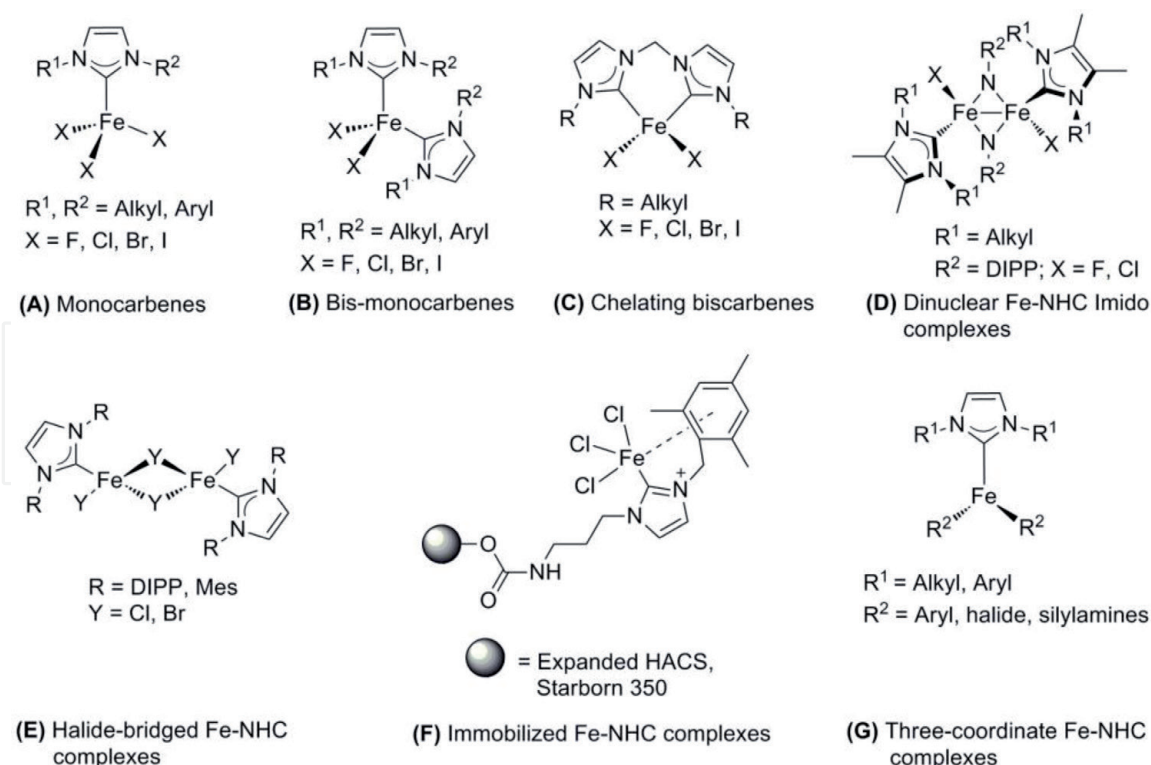


Figure 9.
 (A–G) Halide complexes.

2.4 Scorpionato motifs

Scorpionato-type motifs (**Figure 10C**) means boron linked anionic chelating triscarbene ligands and on complexation with iron results in a new class of Fe-NHC complexes. Therefore, if any iron complex/compound is bearing two scorpionato-type ligands, it will be, (a) coordinated by six carbenes, (b) highly stable, and (c) showing S_6 symmetry along Fe-B-H axis [18]. Different types of scorpionato-type motifs have also been synthesized e.g. tripodal borane NHC iron complexes [18], amine-bridged scorpionato Fe-NHC motifs [18].

2.5 Macrocyclic ligands

Macrocyclic ligands, despite well-investigated other cyclic ligands such as cyclam, porphyrin, on complexation with iron developed a new class of complexes in Fe-NHC coordination chemistry (**Figure 10D**). Their catalytic aspect has been successfully employed in aziridination of alkenes with aryl azides [18, 24].

2.6 Piano stool motifs

The term “piano stool Fe-NHC complexes” states that all such complexes bear both, (a) N-heterocyclic carbene motif and (b) cyclopentadienyl (Cp) ligand. The structural variations in these complexes are well explained by (a) mono- and dimeric piano stool Fe-NHC complexes [18], (b) donor-substituted piano stool Fe-NHC complexes [18], (c) biscarbene-chelated piano stool complexes [18], (d) alkyl piano stool Fe-NHC complexes [18], (e) three coordinate piano stool Fe-NHC complexes [18], and many more [18] (**Figure 10E–G**). These have shown their catalytic activities in C-H bond activation [18], borylation reactions [18, 23], hydrosilylation [18, 25–27], transfer hydrogenation [18], C-N bond formation [18, 24].

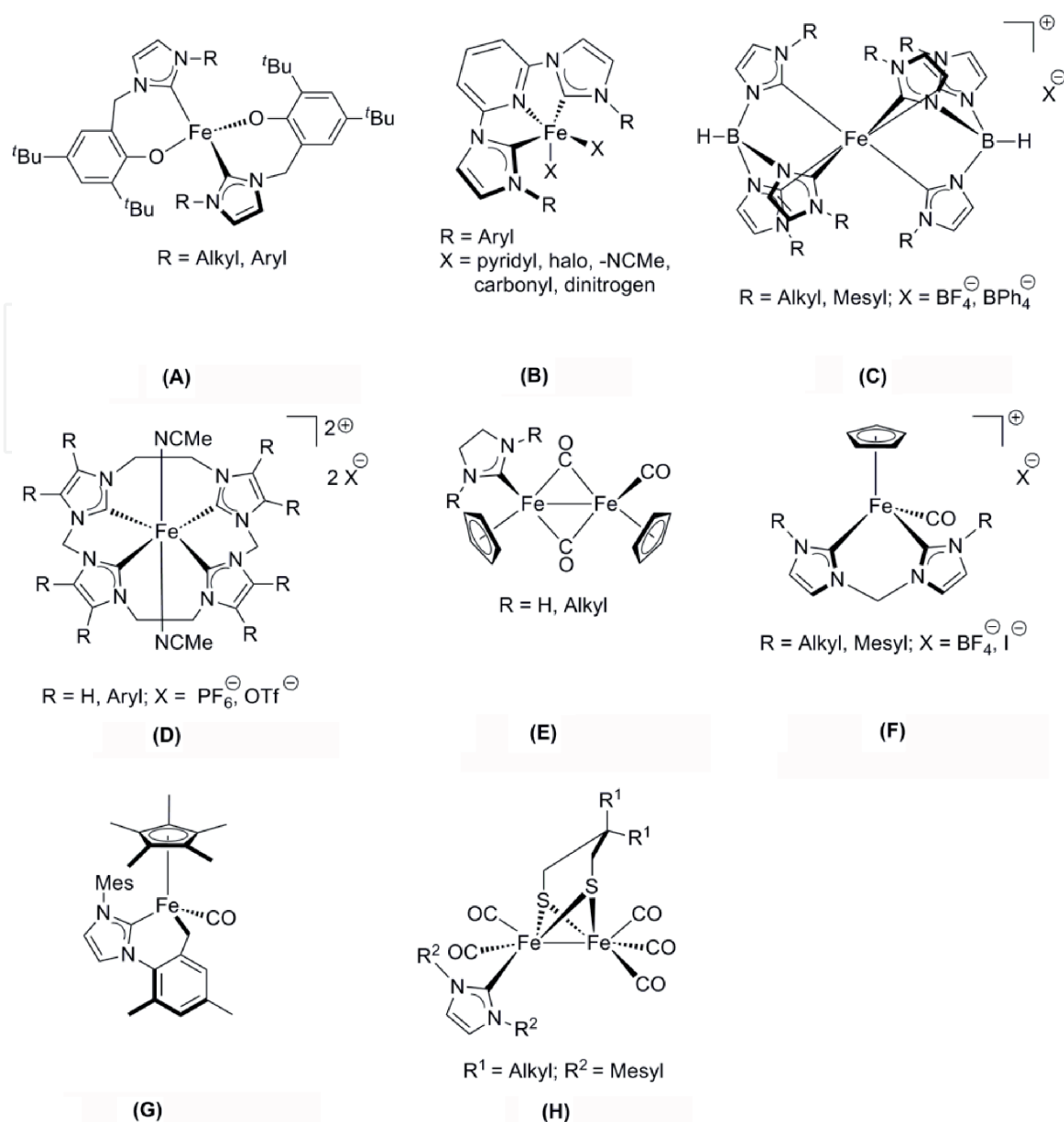


Figure 10.

(A) Donor-substituted NHCs; (B) pincer motifs; (C) Scorpionato motifs; (D) macrocyclic ligands; (E–G) piano stool motifs; (H) iron-sulfur clusters

2.7 Iron-sulfur clusters

Diiron dithiolate complexes (**Figure 10H**) have been reported to mimic the active site of $[\text{FeFe}]$ hydrogenase [18]. Also, the substitution of carbonyl motifs (one or more) in the diiron dithiolate complexes by σ -donor ligands (in this case NHCs) is shown to influence the redox potential of the iron center [18]. Further, donor-substituted NHCs motifs were included in the molecular framework of $[\text{FeFe}]$ hydrogenase model compounds to extend its molecular assembly [18]. Another notable characteristic presence of Fe-NHC complexes bearing iron-sulfur clusters was demonstrated in synthesis of nitrogenase model compounds, which were based on all-ferrous $[\text{Fe}_4\text{S}_4]^0$ [18].

3. Catalysis by Fe-NHC complexes: important transformations

Even if there are a tremendous number of catalysts based on rare/heavy transition metals such as palladium, platinum, ruthenium, rhodium, iridium, and gold

[28–30] are available for various different kind of organic transformations and they are very successful; the scientific community is trying hard to replace these metals by some environment and biological friendly metals because they are highly expensive and very toxic in nature therefore not compatible with biological systems. Iron becomes the obvious choice since it is the most abundant transition metal on the earth's crust, relatively inexpensive, environmentally benign [31] and relatively less toxic to the biological systems [32, 33]. There are several very successful examples of iron-based catalysts like Fischer-Tropsch and the Haber-Bosch processes [34] and are capable of catalysis in numerous different reactions [35, 36]. Reports related to the iron-NHC complexes started coming just after the publication of first metal-NHC complex in 1968, the growth in the research was almost ceased for next three decades and picks up the pace after the success of Grubb's catalyst for various organic transformations and polymerization reactions [20, 37]. Iron-NHC complexes are reported to have found applications in different classes of reactions such as substitution, addition, oxidation, reduction, cycloaddition, isomerization, rearrangement and polymerization reactions (**Figure 11**).

3.1 C-C bond formations

Negishi, Suzuki, and Heck were awarded the Nobel Prize in 2010 for their pioneer work in the area of cross-coupling reactions, as it provides a very effective tool for C-C bond formation. Several different protocols have been reported mainly based on palladium and, to some extent, Ni and copper metal ions. Iron-NHC complex based catalysts have been used for various Kumada-type cross-couplings such as $C(sp^3)-C(sp^2)$, $C(sp^2)-C(sp^3)$, $C(sp^2)-C(sp^2)$, $C(sp^3)-C(sp^3)$ bond formations, and $C(sp^2)-C(sp^2)$ homo-couplings. NHC can either be generated *in situ* in a reaction or a resynthesized iron-NHC complex can be used. Bedford and co-workers, in a first, introduced the NHCs ligands and iron-NHC complexes along with $FeCl_3$ to improve the yield of Kumada-type coupling reactions (**Figure 12A**) [38]. Among

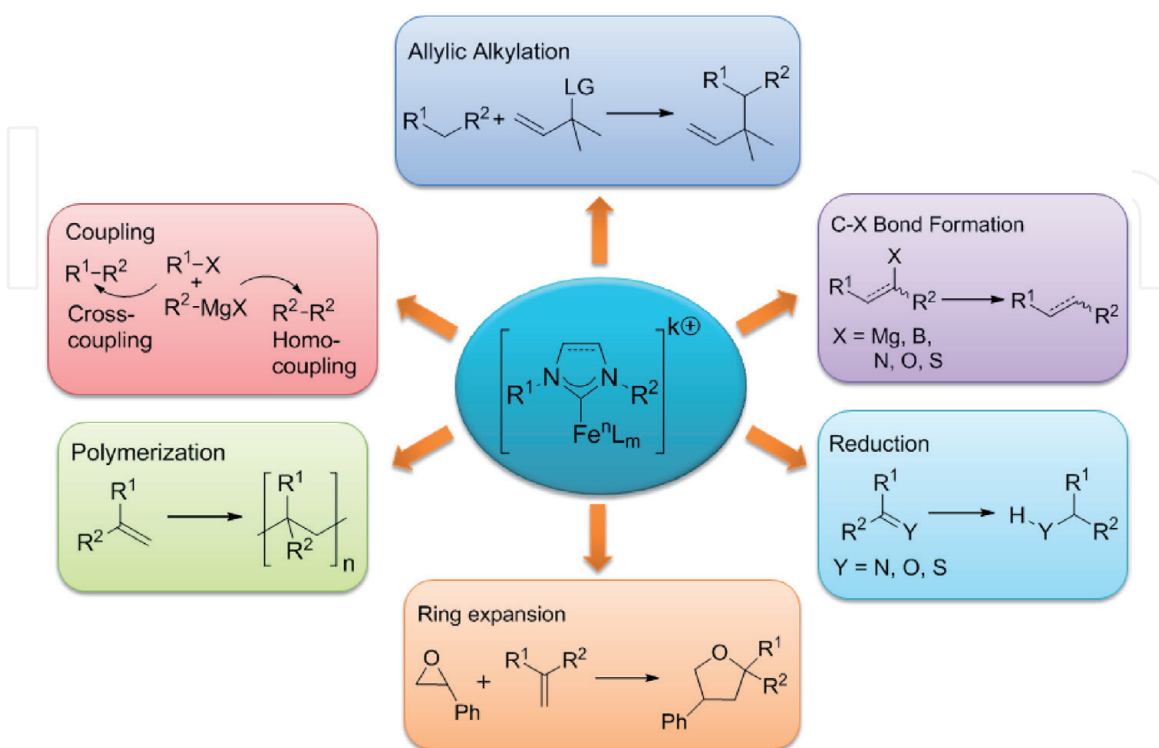


Figure 11.
Important transformations catalyzed by Fe-NHC complexes.

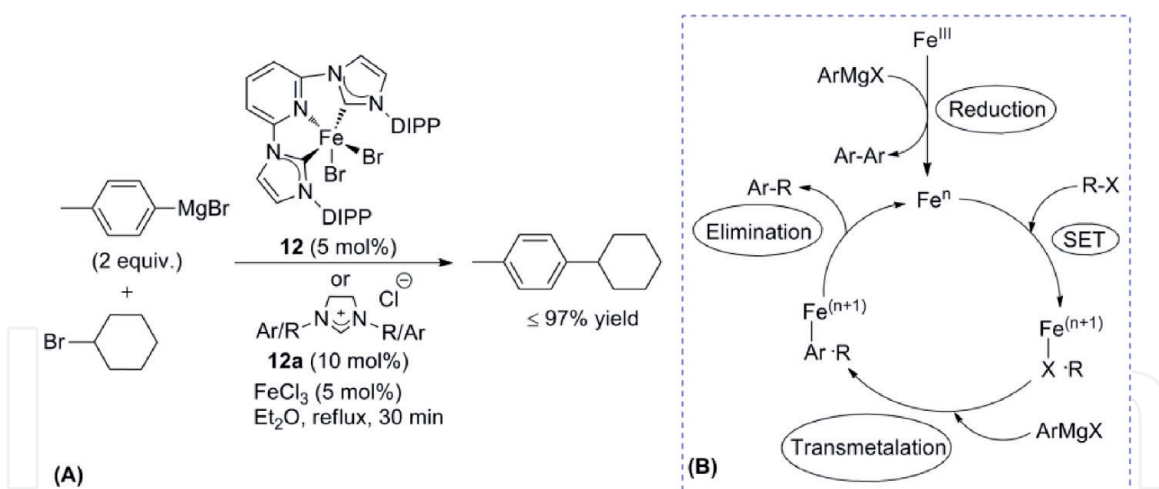


Figure 12.
(A) Aryl Grignard reagents-bromoalkanes cross-coupling [38]; (B) proposed mechanism.

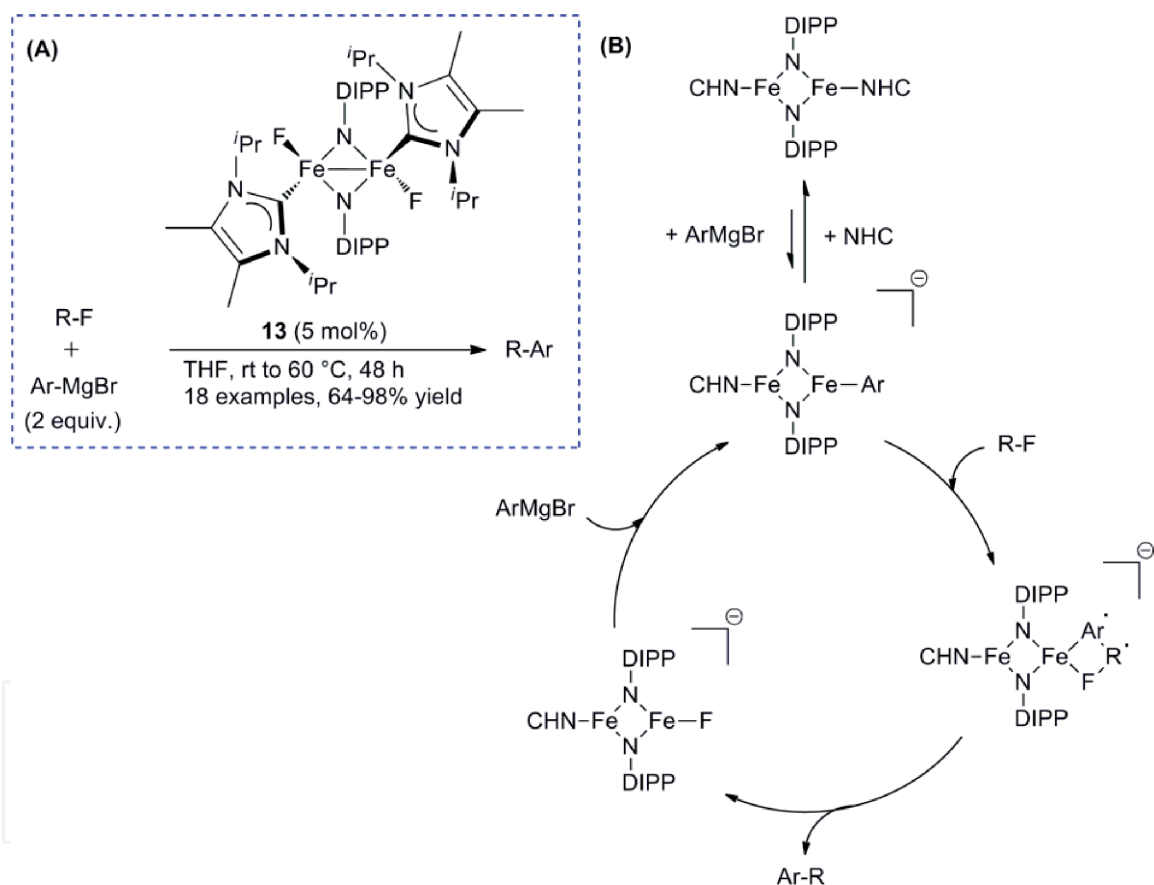


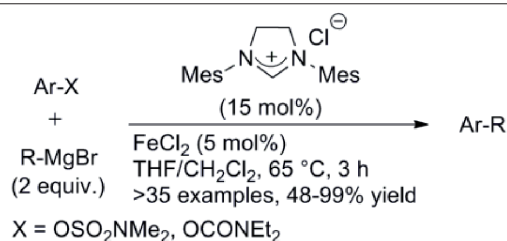
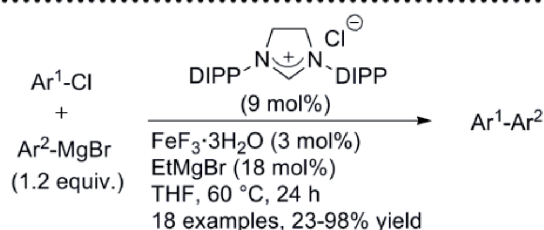
Figure 13.
(A) Primary alkyl fluorides-aryl Grignard reagents Kumada-type coupling [21]; (B) proposed mechanism.

several carbene ligand precursors, *tert*-butylimidazolinium chloride **12a** was found to give the best results (97% yield) and the performance was almost matched by the iron-NHC complex **12** (94% yield).

The proposed mechanism suggests that reaction does not follow the classical oxidative addition mechanism, but rather involves a radical intermediate produced through single electron transfer (SET) (**Figure 12B**) [39, 40]. Reaction mechanism involves the following processes: (i) generation of active catalyst through reduction of Fe(III) to Fe(II, I, or 0), (ii) generation and association (not the oxidative addition) of alkyl radical (R·) with the iron center through SET, (iii) transmetalation, where aryl group is transferred from ArMgX to the iron

center, and (iv) attack of alkyl radical ($R\cdot$) to the aryl group (Ar) leading to the generation of coupled product and the catalyst [38].

It was proved through a control experiment that particularly primary and secondary alkyl halides favor iron-catalyzed reactions, in comparison to most of the Pd or Ni systems, because of their sluggish tendency toward the β -hydride elimination and hence less susceptibility to the olefin formation. Therefore, it plausibly indicated the limitations of the catalytic role of the Fe-NHC complexes, in case of *in situ* formation of an iron NHC complex or the deprotonation of the imidazolium salt. Besides Alkyl bromide, dinuclear Fe-NHC imido complexes such as **13** have been reported to be effective in activating other alkyl halides and most challenging alkyl fluoride (**Figure 13A**). Here again, the use of the substrates such as (fluoromethyl)cyclopropane suggested a radical-mediated mechanistic pathway (**Figure 13B**). The first step is the dissociation of one NHC

Coupling of Alkyl Grignard reagents with Sulfamates and Carbamates^[41]

Aryl-Aryl Coupling^[42]

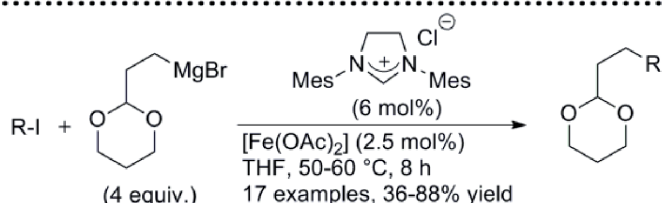
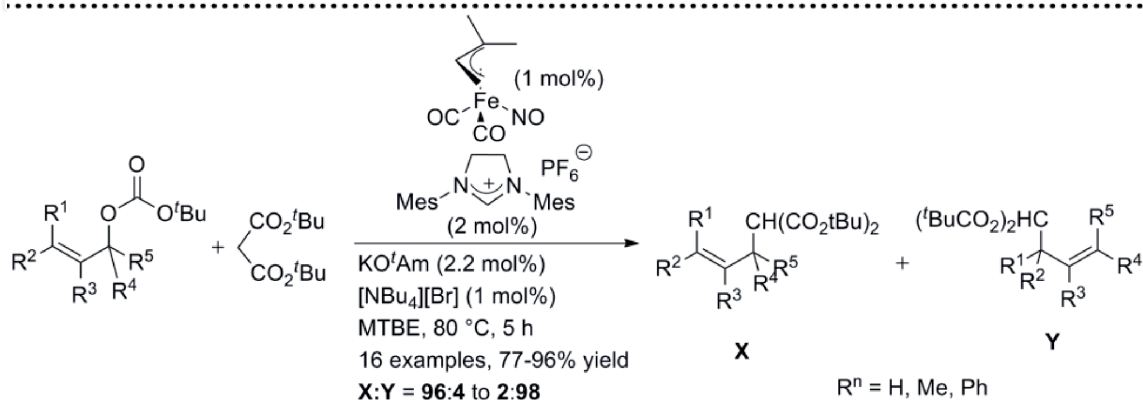
Alkyl-alkyl Cross-Coupling of Grignard Reagents and Alkyl Iodides^[43]Allylic Alkylation with allyl carbonates and pronucleophiles^[44]

Table 1.

Other examples of C-C bond formation and allylic alkylation reactions [41–44].

ligand followed by the second step as transmetalation (note: dinuclear iron imido subunit stays intact during the process). The further mechanism involves the usual mechanistic protocol, which includes firstly the formation of radical species and secondly, attack of the radical on the aryl moiety [21]. Several more iron-NHC complex catalyzed carbon-carbon coupling reactions have been given in **Table 1**.

3.2 Allylic alkylations

In a seminal work by Plietker group [19], allylic alkylation by the catalyst **14** was shown through the reaction of allyl carbonate and a Michael donor resulting into two isomeric products, i.e. (i) Product **X**, through the *ipso* substitution, and (ii) Product **Y**, via a σ - π - σ isomerization (**Figure 14A**). Mechanistic investigation suggests that the product ratio is greatly influenced by the steric crowd around the metal center, created due to the substituents on the nitrogen atoms of NHC moiety. Increased steric crowd hinders the isomerization process and thus favoring *ipso* substitution product **X**. For example, if *tert*-butyl group is present on the N atom of NHC, *ipso* substitution is favored, on the other hand, mesitylene group, which creates less steric hindrance around the metal center, favors isomerized product **Y**. In addition, stronger nucleophilicity of Michael donor favors the *ipso*-substitution. A plausible mechanism is outlined in **Figure 14B**. Few more allylic alkylation reactions are presented in **Table 1**.

3.3 C-X (heteroatom) bond formations

Catalytic C-H bond activation has been one of the major tools to perform effective chemical transformations. Applicability of Fe-NHC complex as the catalyst for C-H bond activation has gained momentum since it can produce the formation of a range of different C-X bonds such as C-N, C-B, C-Mg, and C-S bond. Fe-NHC complex catalyzed C-N bond formation is important because of the three very basic

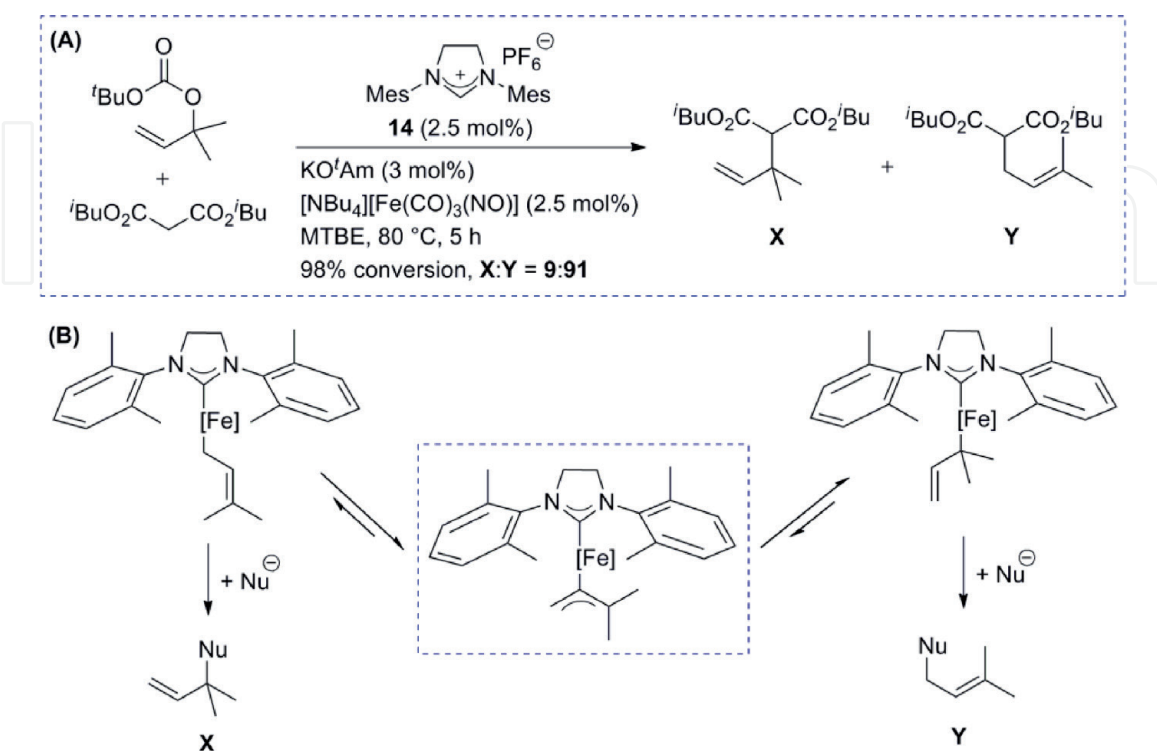


Figure 14.
 (A) (TBA)Fe/NHC catalyzed allylic alkylation [19]; (B) proposed mechanism.

reasons, (a) aziridine based compounds are of medicinal importance and therefore essential for pharmaceutical industry, (b) demand of aziridine derivatives in polymer chemistry as cross-linker agents for two-component resins, and (c) relative to well-known synthesis of *O*-epoxidation analogs, it is hard to synthesize the designer *N*-building blocks. Catalytic aziridination of alkenes by using Fe-NHC complex **15**

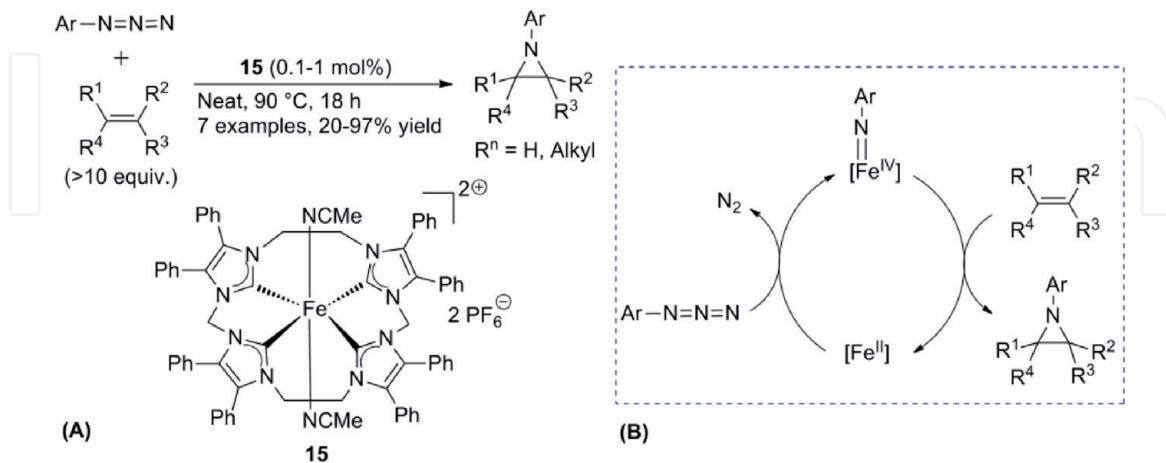
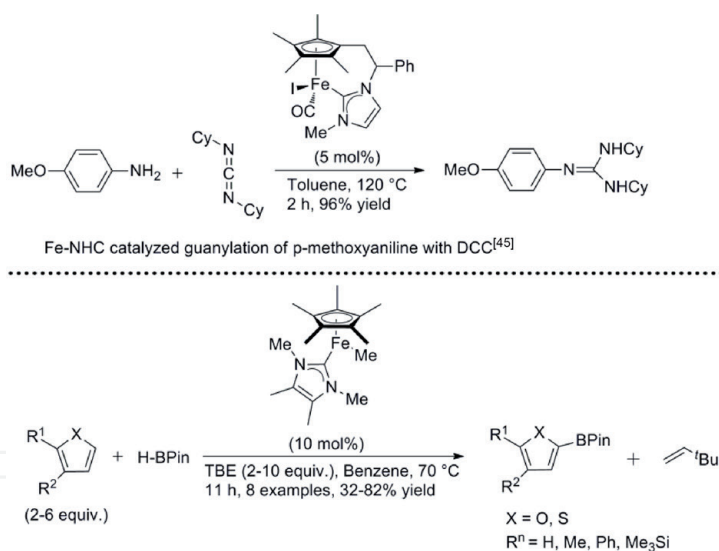
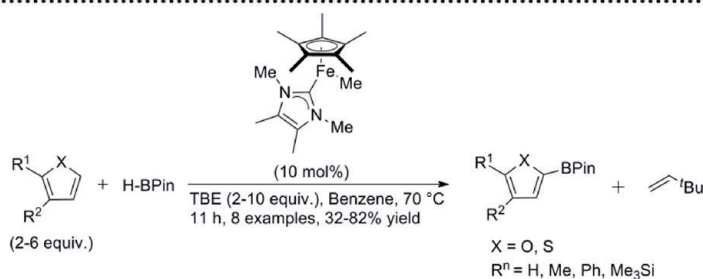


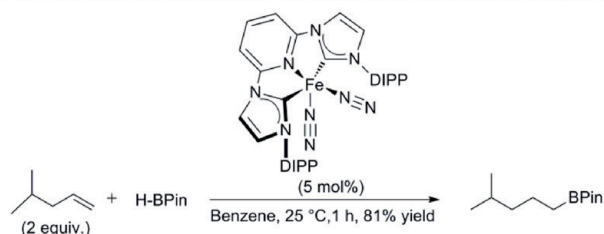
Figure 15. (A) Fe-NHC catalyzed aziridination of alkenes [24]; (B) proposed mechanism.



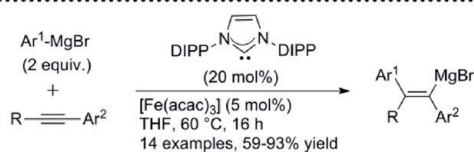
Fe-NHC catalyzed guanylation of *p*-methoxyaniline with DCC^[45]



Borylation of furans and thiophenes catalyzed by Fe-NHC complex^[23]



Hydroboration of alkenes catalyzed by low-valent Fe-NHC complex^[46]



Fe-NHC catalyzed arylmagnesiation of acetylenes^[47]

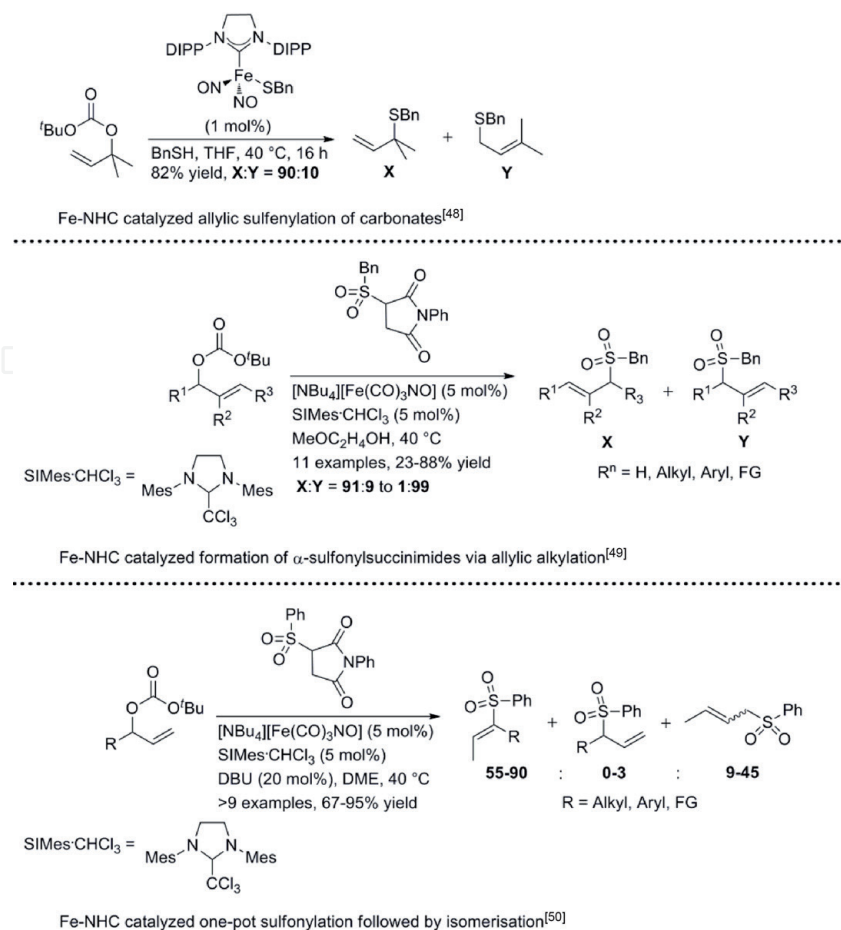


Table 2.
Other examples of C-X bond formations [23, 45–50].

(0.1–1 mol%) as the catalyst was published by Jenkins et al. [24] to form respective aryl-substituted aziridines by treating aryl azides with various substituted alkene (**Figure 15A**). As proposed, the reaction involved the formation of a key and highly reactive intermediate Fe(IV) imido complex (**Figure 15B**). Few more C-X bond formation reactions are presented in **Table 2**.

3.4 Reduction reactions

There are several reports on the reduction of alkenes via silylation using iron-NHC complexes. Royo group was first to show such conversion using piano stool type complex **16** (**Figure 16A**) [25]. The reaction is sensitive to the type of substituent present at para-position in the aromatic ring of the reactant, e.g. quantitative yields for reactions of *p*-aryl-substituted aldehydes and alkyl-substituted aldehydes or ketones remained unreactive. Another piano stool type complex **17** reduces ketones and aldehydes into the corresponding alcohols very efficiently (**Figure 16B**) [26]. Same catalyst **17** can reduce the carbonyl group of various amides in moderate to excellent yields (**Figure 16C and D**) [27]. In both cases, irradiation of visible light is crucial for the reported effective conversions, where PhSiH_3 works as the hydride source. Catalyst shows differential reactivity with the primary, secondary and tertiary amides. Secondary and tertiary amides give usual conversion of carbonyl group into alcohol, while primary amide converts into nitrile compound. Cyclic amides have to be protected before reduction; otherwise a mixture of products forms.

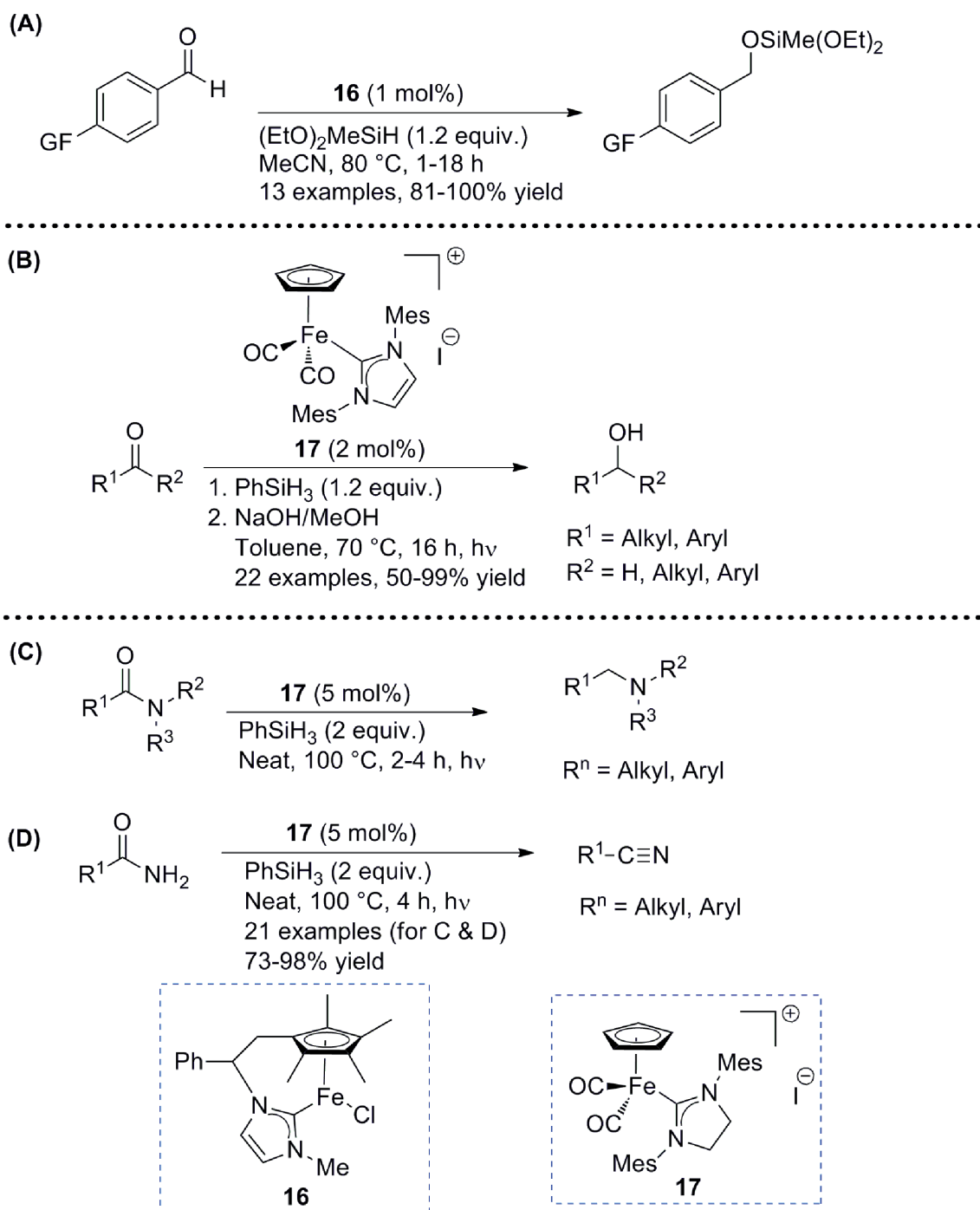


Figure 16. Hydrosilylative reductions of (A) benzaldehyde derivatives [25]; (B and C) substituted and primary amides, respectively [27].

Various recently reported iron-NHC complex catalyzed reduction reactions are summarized in **Table 3**.

3.5 Cyclization reactions

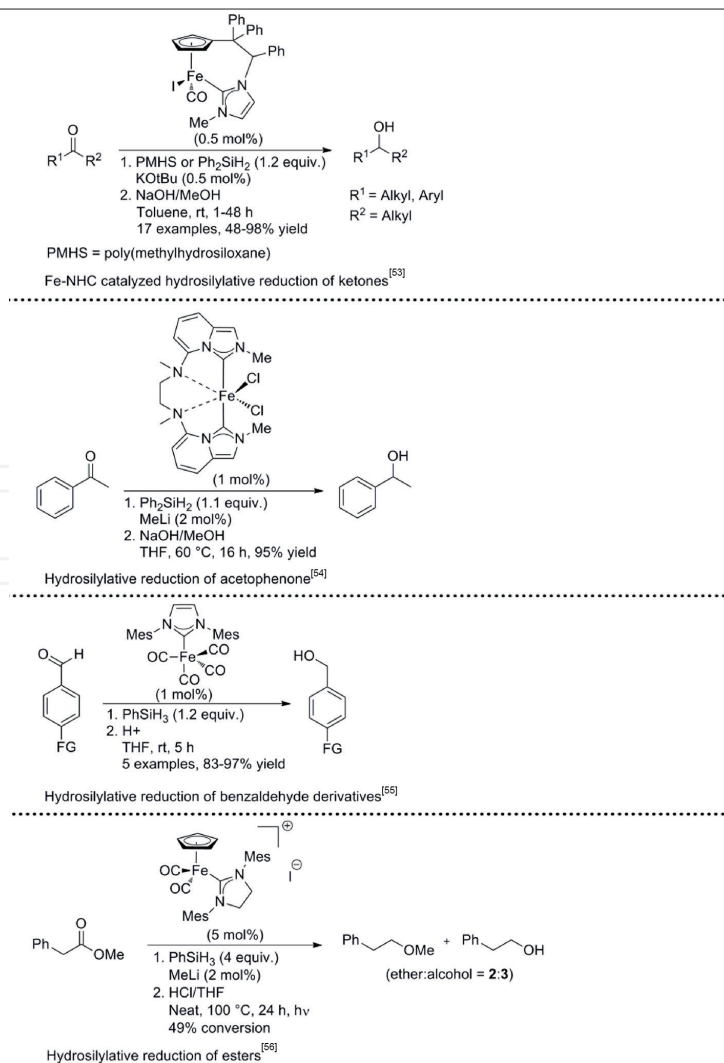
Fe-NHC catalyzed ring expansion of the epoxides with functionalized alkenes presents a very intriguing case because cyclic structures are of great importance in various fields such as the pharmaceutical industry, fine chemicals, agriculture, etc. Fe-NHC catalyzed such reactions not only have shown functional group tolerance but also high chemo- and regioselectivity.

Hilt et al. [51] used a mixture of FeCl_2 , phosphine ligands and *in situ* generated free NHCs, **18** and performed reaction under reductive conditions using Zn and NEt_3 (**Figure 17A**). The reaction mechanism demonstrates the first step as a SET (single-electron transfer) in epoxide ring-opening, the second step as the formation of an elongated alkoxy radical via reaction between formed radical intermediate and added alkene, and the final step as a BET (back-electron transfer), which gave the desired expanded cyclic product via a zwitterionic intermediate cyclization (**Figure 17B**).

3.6 Polymerization

So far, the application of Fe-NHC complexes have not been much explored in the area of polymerization [52]. Grubbs has first reported the use of Fe-NHC complex **19** as the catalyst in atom transfer radical polymerization (ATRP) reaction of styrene and methyl methacrylate (**Figure 18**) [20]. The reaction shows pseudo first-order kinetics, a decent control of radical concentration, and polydispersity index (PDI) near 1.1.

Shen and co-workers have reported the ring-opening polymerization (ROP) reaction of ϵ -caprolactone by using Fe-NHC complex **20** as the catalyst [22]. Even though reaction suffers some side reaction of transesterification, polymerization progresses with quantitative conversion and moderate number average molecular weight distribution (**Figure 19**).



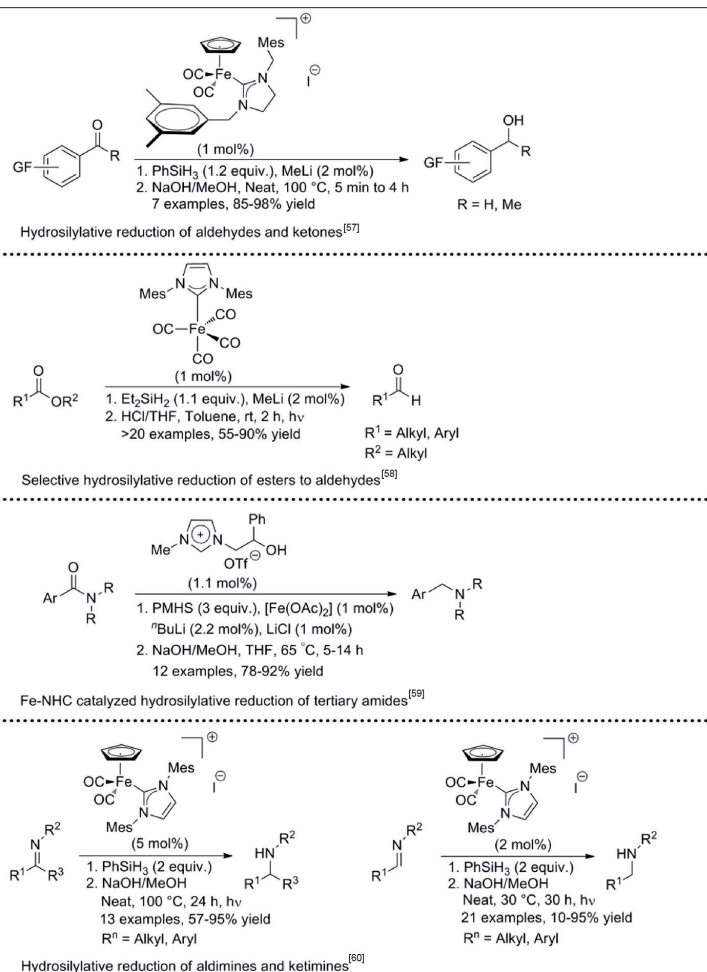


Table 3.
Other examples of reduction reactions [53–60].

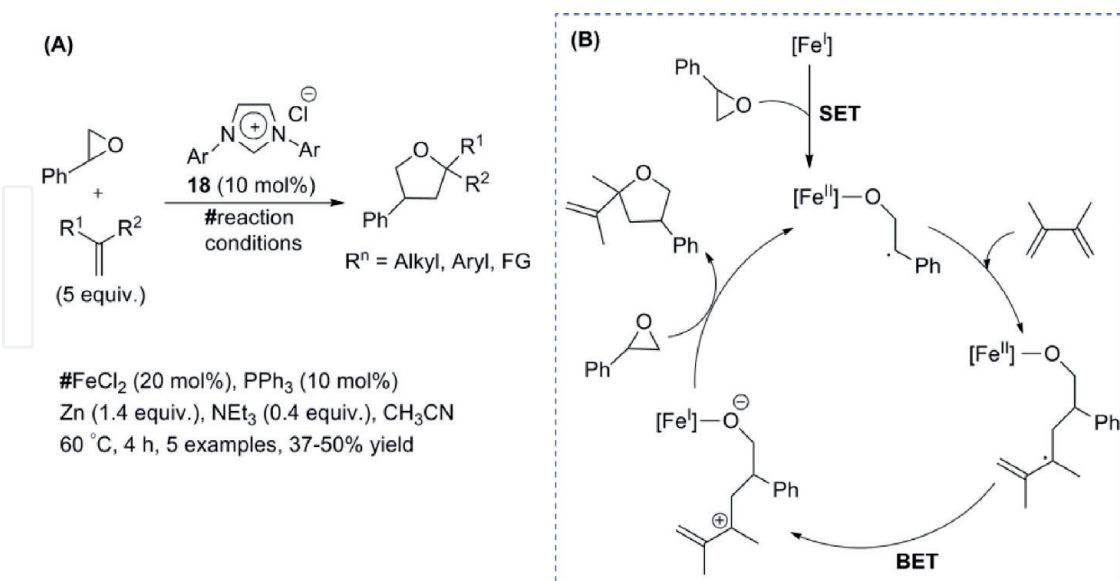


Figure 17.
(A) Fe-NHC catalyzed epoxide ring expansions [51]; (B) proposed mechanism.

4. Conclusion

Iron will remain a metal of choice for the replacement of all the heavy metal ions currently being used for the application of catalytic processes for the obvious reason

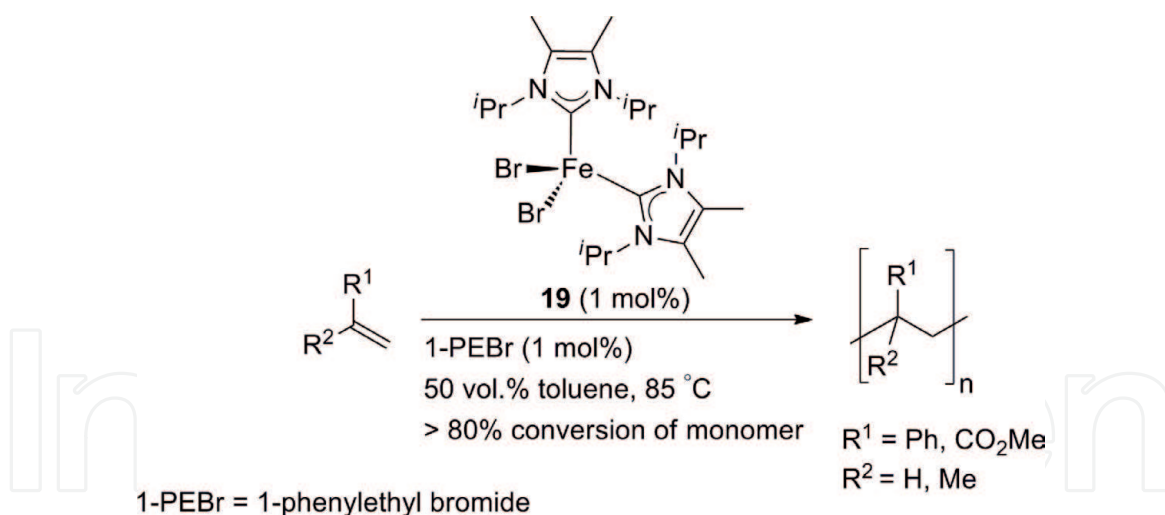


Figure 18.
 Atom transfer radical polymerization (ATRP) of olefins [20].

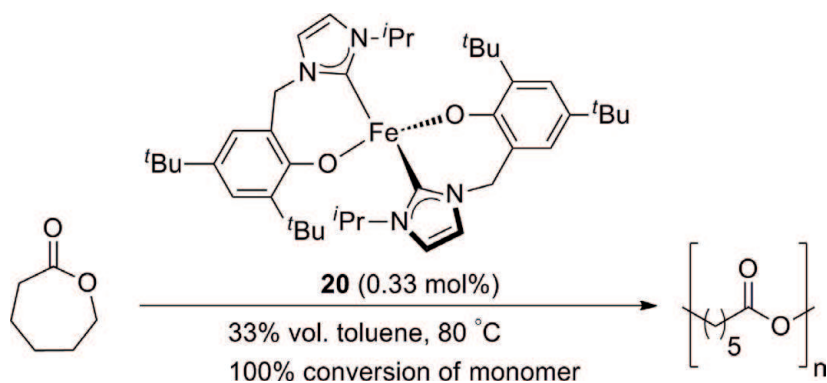


Figure 19.
 Ring-opening polymerization of ϵ -caprolactone [22].

of it being economical, very high natural abundance, environmentally benign and more importantly biologically compatible. Earlier, several iron-based complexes have enjoyed their success in many processes like Fischer–Tropsch and the Haber–Bosch processes, but the progress of iron-NHC complexes has gained momentum only after the success of Grubb’s catalyst at the onset of this century and now the number of published articles is growing with every passing year. The importance of Fe-NHC complexes can be evaluated from the aforementioned fact that they have found applicability in diverse fields from academia (e.g. biomimetic studies, various intriguing chemical transformations) to industries (e.g. pharmaceutical industry). The existing and ever possible versatility of (i) various structural motifs with different oxidation states, (ii) their flexible coordination geometries before and after the reaction, and (iii) substitution patterns in the iron N-heterocyclic carbene complexes along with their potential economic and toxicity benefits present an exciting scenario for the upcoming generation.

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Conflict of interest

Authors have no conflict of interests to declare.

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