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Reactivity and Properties of Metal Complexes Enabled by Flexible and Redox Active Ligands with a Ferrocene Backbone

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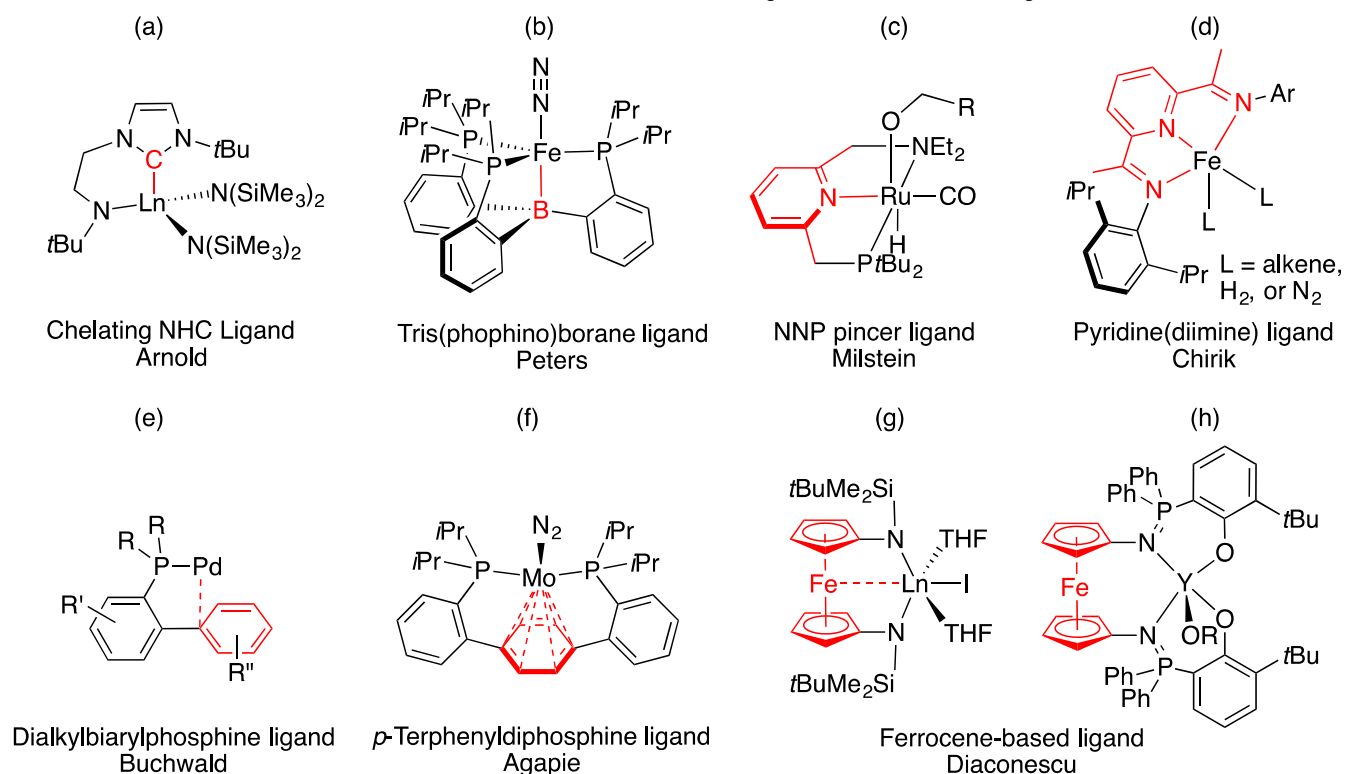
ABSTRACT: Our group has focused on the organometallic chemistry of rare-earth metals and actinides for a decade. By installing ferrocene diamide ligands at electropositive metal centers, we have been able to disclose unprecedented reactivity toward aromatic N-heterocycles, arenes, and other small molecules such as P_4. Systematic studies employing X-ray crystallography, spectroscopy, cyclic voltammetry, and DFT calculations revealed that the ferrocene backbone could stabilize the electron-deficient metal through a donor-acceptor type interaction. Most noteworthy is that this interaction can be readily turned on or off by the addition or removal of a Lewis base. In addition to its flexible coordination, the redox active nature of the ferrocene backbone enabled us to explore redox-switchable transformations. The introduction of ferrocene-based ligands into organolanthanide chemistry not only helped to study intriguing fundamental problems but also led to fruitful chemistry including small molecule activation and controlled co-polymerization reactions.

Introduction

Organometallic chemistry is an interplay between "inorganic" metals and "organic" ligands. With the rapid development of this field of research, the line between inorganic and organic chemistry has become blurred. Albeit most elementary steps take place at the metal center(s), ligands play a key role in facilitating a desired transformation. For example, for homogenous catalysis, ligands promote a reaction by stabilizing the metal in solution. Furthermore, most transformations require multiple steps, in which the metal center may be in different oxidation or spin states, and/or coordination numbers. One way to accommodate those changes is to introduce a coordinatingly flexible ligand. Such a ligand usually contains multiple donor sites: among them, some strongly bind to the metal and anchor it to prevent dissociation, while others form weak interactions with the metal that can be readily cancelled or reestablished upon the addition or removal of an external donor. Simplistically, rare-earth and early transition metals are hard acids and form strong bonds with hard donors such as oxygen and nitrogen and bind only weakly to soft donors, while late transition metals prefer bonding to soft donors like phosphines and N-heterocyclic carbenes over hard donors.

An obvious strategy for the design of a coordinatingly flexible ligand is to combine both hard and soft donors in a single molecule. Noticeable examples include N-heterocyclic carbenes with a tethered anionic anchor (Chart 1a)[1, 2] and XP_3 type (X = B or N) triphosphine ligands with an additional donor X in the backbone (Chart 1b).[3, 4] When the former coordinate to electropositive metals, the N-heterocyclic carbene acts as a labile donor that can readily dissociate.[5] When the latter bind to late transition metals, the metal-X distance may vary according to the change in the coordination environment around the metal.[4, 6] In addition to variations in the coordination environment, the oxidation state of the metal can also change. This change can have a large impact on the metal-ligand interaction and requires the supporting ligand to be robust enough to remain bound to the metal. In order to mitigate such issues, redox non-innocent ligands can be used. These ligands usually contain a conjugated π system that has an accessible HOMO and LUMO for donating or accepting electrons. This strategy has been found exceptionally successful for aiding multi-electron processes such as dioxygen evolution and dinitrogen fixation since it prevents an abrupt change of electron density at the metal center; in this way, a lower energy barrier may be achieved for the formation of certain multiple bonds or activation processes.[7, 8]

(a) Chelating NHC Ligand
Arnold

(b) Tris(phophino)borane ligand
Peters

(c) NNP pincer ligand
Milstein

(d) Pyridine(diimine) ligand
Chirik

(e) Dialkylbiarylphosphine ligand
Buchwald

(f) p-Terphenyldiphosphine ligand
Agapie

(g) (h) Ferrocene-based ligand
Diaconescu

Chart 1: Representative examples of metal complexes containing flexible and non-innocent ligands. The flexible or non-innocent parts of the ligands are highlighted in red as well as the metal-ligand interaction.

Ideally, a ligand that has both coordination flexibility and a redox active nature may serve as an excellent candidate for stabilizing otherwise transient species, promoting small molecule activations and facilitating catalytic transformations. An example worth mentioning is a class of pincer type ligands with an aromatic backbone (most commonly, pyridine) and two neutral donor arms that can be imine, amine, phosphine, N-heterocyclic carbene, etc.[9-12] For example, Milstein and coworkers demonstrated the

role of PCP and PNP pincer ligands in catalysis and small molecule activation and proposed mechanisms in which metal-ligand cooperation plays a major role (Chart 1c).[13-21] In addition, Chirik and coworkers exploited the potential of base metals in catalytic transformations by using flexible and redox non-innocent ligands to overcome the limitation of first row transition metals that usually undergo single electron processes (Chart 1d).[22-25] Besides traditional phosphine and nitrogen donors, an arene is suitable for metal-ligand cooperation as well: first, the coordination mode of the arene can vary from η^6 to η^2 according to the degree of delocalization.[26, 27] Second, while the HOMO of an arene can act as a σ or π donor, its LUMO has the appropriate symmetry and energy to engage in back-donation with electron-rich metals.[28] In some cases, a metal-to-ligand charge transfer can result in partial reduction of the arene and, thus, provide an electron reservoir for the metal.[29, 30] Therefore, in theory, arenes could serve as flexible and redox non-innocent ligands. In practice, because the arene-metal interaction is usually not robust enough, the arene is usually incorporated into the backbone of the supporting ligand. A successful case is a class of dialkylbiarylphosphine ligands developed by the Buchwald group for palladium catalyzed coupling reactions (Chart 1e).[31] The biaryl moiety has been found critical to improve the catalytic activity of palladium through reversible coordination of the remote phenyl ring. The biaryl unit provides a versatile platform for chemical modifications to tune the electronic and steric properties of the ligand, which, in turn, determine the catalytic reactivity of the palladium complex. The charge transfer from palladium to the arene is minimal during the catalytic cycle due to the dual stability of Pd(0) and Pd(II).[32] However, in another case demonstrated by Agapie et al., a *para*-terphenyl diphosphine ligand supporting bimetallic or monometallic complexes, the charge transfer from the first row transition metals to the middle phenyl ring can result in its dearomatization (Chart 1f).[33, 34] This unusual phenomenon allowed unprecedented reactivity including the change of up to five oxidation states of a dinitrogen complex and four-electron deoxygenative reductive coupling of carbon monoxide at a single metal site.[35]

Our group has taken a different approach in order to achieve the goal of coordination flexibility and redox activity (Chart 1g, h).[27-29, 36-87] Instead of using a purely organic ligand, we reasoned that an organometallic ligand should serve as an excellent candidate. Such a ligand needs to fulfill the following requirements: (1) the organometallic part should be chemically inert under common reaction conditions; (2) the metal should be redox active; (3) the organometallic fragment should be able to act as a weak donor. A metallocene seems to be a good candidate to meet all three requirements. Amongst metallocenes, ferrocene, Cp_2Fe ($Cp = \eta^5\text{-}C_5H_5$) stands out for the following reasons: (1) it is chemically robust; (2) it has a well-behaved reversible redox event, $Cp_2Fe^{0/1+}$; (3) it is electron-rich and, therefore,

can form a weak donor-acceptor interaction with an electron deficient metal center. Probably more important, from a synthetic perspective, ferrocene is inexpensive and available in large quantities, while chemical modifications of ferrocene are well established. Herein, we are going to describe our efforts in exploiting ferrocene-based ligands in organometallic rare-earth chemistry. The content is organized in the following order: A. Synthesis and electronic properties of ferrocene-based ligands; B. Synthesis of rare-earth metal complexes supported by ferrocene-based ligands; C. C-H activation, dearomatization, and ring-opening reaction of aromatic N-heterocycles; D. Reduction chemistry with π ligands and small molecule activation; E. Redox-switchable catalysis enabled by redox active metals and ligands. Since large parts of section C and some part of section D have been previously reviewed,[27, 28, 72, 80] we are not going to discuss details but rather highlight the role of ferrocene-based ligands in enabling new reactivity and properties.

Results and Discussion

A. Synthesis and Electronic Properties of Ferrocene-based Ligands

Our group focused on a series of ferrocene-based ligands that can be categorized into two groups: bidentate ferrocene diamide ligands (NN^{fc}, fc = 1,1′-ferrocenediyl) and tetradentate diaryloxide ligands ($OEEO^{fc}$, E = N or S) (Scheme 1). NN^{fc} ligands (labeled in blue in Scheme 1) could be obtained from a common intermediate, $fc(NH_2)_2$ through silylation ($H_2(NN^{TMS})$, $fc(NHSiMe_3)_2$;[88] $H_2(NN^{TBS})$, $fc(NHSitBuMe_2)_2$;[83] $H_2(NN^{DMP})$, $fc(NHSiPhMe_2)_2$),[50] Buchwald-Hartwig amination ($H_2(NN^{XYL})$, $fc(NHC_6H_3Me_2\text{-}3,5)_2$;[56] $H_2(NN^{MES})$, $fc(NHC_6H_2Me_3\text{-}2,4,6)_2$),[89] or condensation followed by reduction ($H_2(NN^{NP})$, $fc(NHCH_2tBu)_2$)[90]. Regarding $OEEO^{fc}$ ligands (labeled in red in Scheme 1), $H_2(salfen)$ (1,1′-di(2,4-di-*tert*-butyl-salicylimino)ferrocene)[91] and $H_2(salfan)$ (1,1′-di(2,4-di-*tert*-butyl-6-*N*-methylmethylenephenol)ferrocene)[43] were obtained from the condensation of 1,1′-$fc(NH_2)_2$ and 3,5-di-*tert*-butylsalicylaldehyde, while $H_2(phosfen)$ (1,1′-di(2-*tert*-butyl-6-diphenylphosphiniminophenol)ferrocene) was synthesized by a Staudinger reaction between 1,1′-$fc(N_3)_2$ and 2-*tert*-butyl-6-diphenylphosphinophenol.[59] $H_2(thiolfan)$ (1,1′-di(2,4-di-*tert*-butyl-6-thiomethylenephenol)ferrocene) and $H_2(thiolfan*)$ (1,1′-di(2,4-di-*tert*-butyl-6-thiophenol)ferrocene) were prepared from 1,1′-dilithioferrocene.[43] The synthesis of 1,1′-$fc(N_3)_2$ (featured in red) and 1,1′-$fc(NH_2)_2$ (featured in blue) can be traced back to 1961 to Pauson and coworkers, who published it shortly after the discovery of ferrocene.[92] Two years later in 1963, Russian chemists reported the synthesis of $fc(N_3)_2$ and $fc(NH_2)_2$.[93] However, it was not until 2000, when Arnold et al. reported an improved synthesis of $fc(NH_2)_2$, that easy access to large quantities of $fc(N_3)_2$ and $fc(NH_2)_2$ was possible (Scheme 1).[94]

Scheme 1: Synthesis of ferrocene-based pro-ligands and key intermediates: H₂(NN^fc) type: H₂(NN^TBS), H₂(NN^TMS), H₂(NN^DMP), H₂(NN^XYL), and H₂(NN^MES); H₂(OEEO^fc) type: H₂(salfen), H₂(phosfen), H₂(salfan), H₂(thiolfan), and H₂(thiolfan*). Ligand labels are highlighted in red.

We performed a systematic experimental and computational study on the series of H₂(NN^fc), H₂(NN^TMS), H₂(NN^TBS), H₂(NN^DMP), H₂(NN^NP), H₂(NN^XYL), and H₂(NN^MES), including the parent H₂(NN^H) (fc(NH₂)₂), using various methods, such as cyclic voltammetry, electronic absorption spectroscopy, vibrational spectroscopy, X-ray crystallography, and DFT calculations, with a focus on the redox event between the neutral and one-electron oxidized

compound.[50] All $H_2(NN^{fc})$ showed a reversible or quasi-reversible redox event for $[H_2(NN^{fc})]^{0/+}$ at a negative potential (ranging from -0.60 to -0.73 V versus $Cp_2Fe^{0/+}$). DFT calculations showed that the neutral $H_2(NN^{fc})$ adopted an eclipsed geometry for the two cyclopentadienyl (Cp) rings, while the oxidized $[H_2(NN^{fc})]^+$ was found to prefer a staggered geometry. Another interesting feature upon oxidation was the change of the Fe-Cp$_{centroid}$ distance: instead of shortening upon oxidation, it actually elongated by ca. 0.07 Å for most $H_2(NN^{fc})$. This elongation contradicts the general trend of ionic interactions that usually strengthen as the metal oxidation state increases, but is consistent with bond weakening in covalent interactions. This change is more significant in $H_2(NN^{fc})$ than in the parent ferrocene (ca. 0.02 Å) and is accompanied by the strengthening of the C_{ipso}-N interaction (shortening of ca. 0.05 Å). Overall, the substituents on nitrogen were found to have only a minimal impact on the electronic properties of the ligand, however, they could significantly change its steric profile. Among NN^{fc} ligands, NN^{TBS} was most commonly used because of its improved solubility compared to NN^{TMS} and lack of decomposition pathways compared to those featuring an aryl substituent such as NN^{MES} and NN^{XYL}.[62] The presence of *tert*-butyl groups was also instrumental to help the crystallization process that was essential for X-ray diffraction studies.

In the case of $H_2(OEEO^{fc})$, the one electron oxidation event takes place at a more positive value (-0.10 to -0.30 eV) compared to $H_2(NN^{fc})$.[43, 59-61] We first introduced a Schiff base derivative, salfen, to cerium and yttrium[78] and later developed the phosfen ligand that could be cleanly oxidized by a ferrocenium oxidant to enable redox controlled catalysis.[61] The salfan, thiolfan and thiolfan* ligands were found to fit group 4 metals well and have been exploited in redox-switchable copolymerization processes.[43]
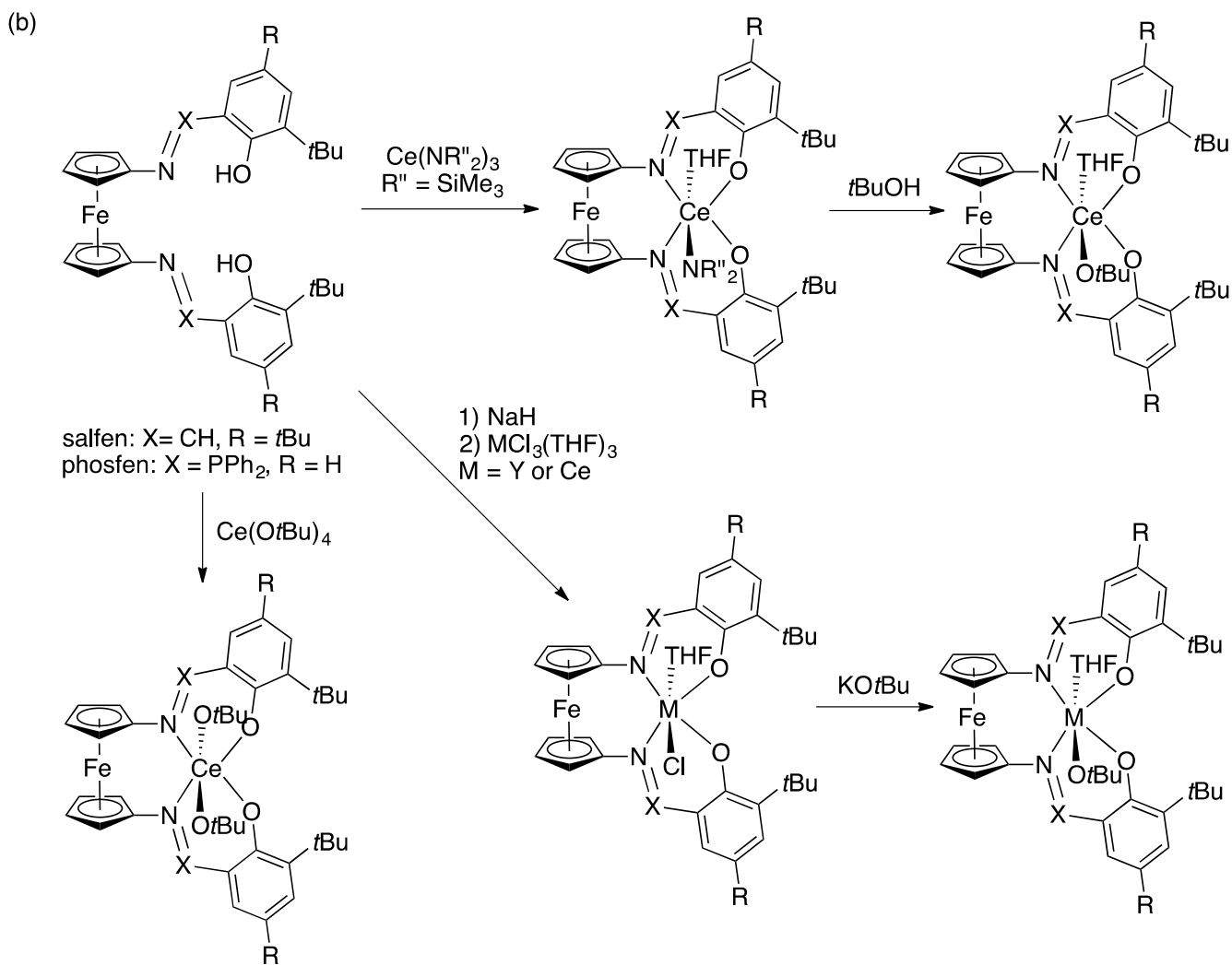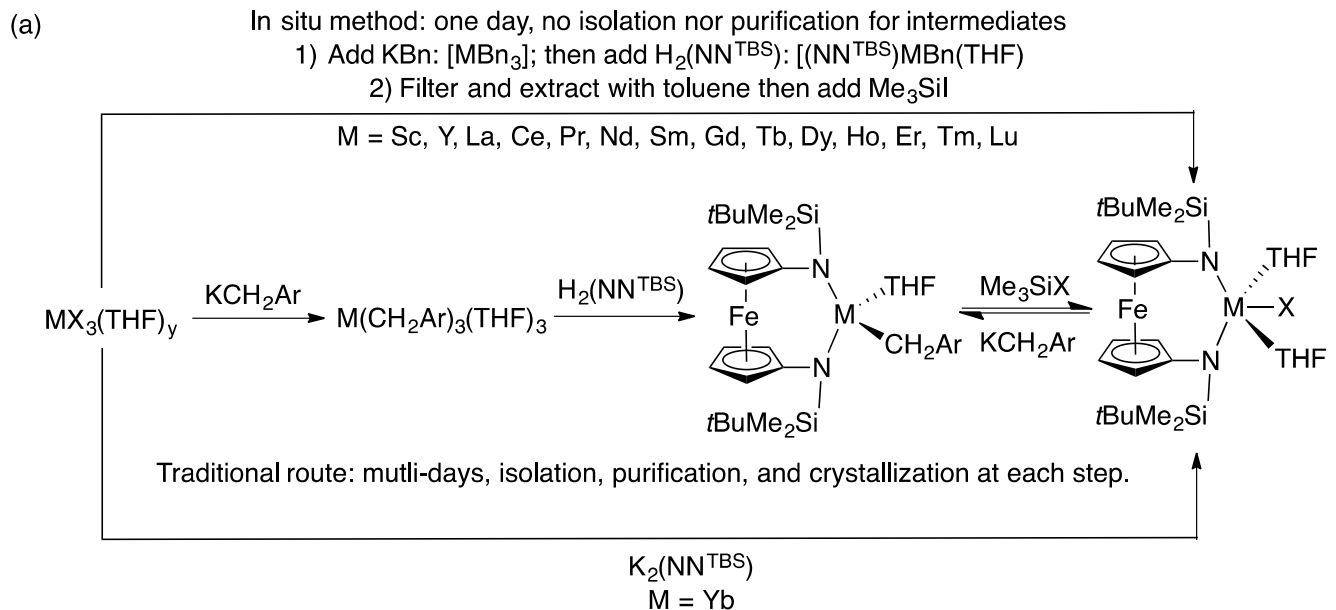
B. Synthesis of Rare-Earth Metal Complexes Supported by Ferrocene-based Ligands

The synthesis of rare-earth metal complexes supported by ferrocene-based ligands can be divided into two groups based on the type of ligand: for the ferrocene diamide ligands NN^{fc}, an alkane elimination reaction between $H_2(NN^{fc})$ and rare-earth metal tribenzyl precursors was found to be the most straightforward route without contamination of side products for most rare-earth metals (except the redox active europium and ytterbium);[29, 41, 46, 65, 81, 82] for the tetradentate ligands $OEEO^{fc}$, various methods, including amine or alcohol elimination and salt metathesis, could be employed to obtain the desired rare-earth metal complexes.[43, 59, 78]

(NN^{fc}): Initially, we sought out to employ salt metathesis between $K_2(NN^{fc})$ and $MX_3(THF)_y$ (M = rare-earth metal, X = Cl or Br, y = 3-4) and found that the reaction was poorly reproducible and usually accompanied by a side product, the bis-ligand-adduct $K[(NN^{fc})_2M]$, which was difficult to remove.[81] At the same time, we and other groups independently published protocols to prepare key metal benzyl synthetic intermediates, $M(CH_2Ar)_3$ (M = Sc, Y, La, and Lu, Ar = Ph, 3,5-$C_6H_3Me_2$), from MX_3 (X = Cl, Br),[95-98] which, in turn were obtained directly from metal oxides.[99] The acid-base reaction between $M(CH_2Ar)_3$ and $H_2(NN^{fc})$ afforded the desired rare-earth metal alkyl product $(NN^{fc})M(CH_2Ar)(THF)$ in high yield and purity. The corresponding metal halide species, $(NN^{fc})MX(THF)_x$ (X = Cl or I, x = 1 or 2), were obtained by treating $(NN^{fc})M(CH_2Ar)(THF)$ with excess Me_3SiX. One drawback of this synthetic protocol is the instability of rare-earth metal tribenzyl complexes. Therefore, we developed an in situ method to prepare $(NN^{fc})M(CH_2Ph)(THF)$ or $(NN^{fc})MX(THF)_x$ directly from MX_3 without the need to purify or isolate an intermediate.[41, 46] This in situ method was much more efficient: the preparation time was reduced to 1 day from 1 week and the overall yield was improved for all rare-earth metals, Scheme 2a. In addition, it became particularly useful when we decided to extend our studies from diamagnetic rare-earth metals to the whole lanthanide series: some metal trisalkyl species were not stable at room temperature and the intrinsic paramagnetism prevented a routine NMR characterization study. Albeit efficient and high yielding, the in situ method has its limitations: it could not be applied to some redox active metal centers, namely europium and ytterbium. This is due to the reducing nature of KCH_2Ph and oxidative character of the Eu(III) and Yb(III) ions. For these ions, we went back to salt metathesis and obtained a high yield of the desired ytterbium complex, $(NN^{fc})YbCl(THF)$, without side product contamination, when an exact stoichiometry and slow addition of the reagents were properly employed. However, the strong oxidizing potential of Eu(III) made the synthesis of $(NN^{fc})EuX(THF)_x$ complexes elusive so far.[41] The easy access to $(NN^{fc})MX(THF)_x$ for most rare-earth metals enabled us to explore the generality as well as the individuality of the whole lanthanide series.

($OEEO^{fc}$): Several synthetic routes could be applied to obtain rare-earth metal complexes supported by $OEEO^{fc}$ ligands, including amine elimination from metal triamides, alcohol elimination from homoleptic metal alkoxides, and salt metathesis between the deprotonated pro-ligand and a metal halide (Scheme 2b).[59-61, 78] Due to the high acidity of the phenolic proton of $H_2(OEEO^{fc})$, the installation of the metal fragment was facile; the choice of synthetic routes was mainly based on the desired composition of the pre-catalysts used for polymerization and the ease of availability of a metal precursor. Group 4 metal complexes supported by salfan, thiolfan, and thiolfan* ligands were prepared in a similar way using $Zr(OtBu)_4$ or $Ti(OiPr)_4$ as metal precursors.[43] In addition, the group 13 metal complex (salfen)In(OtBu) was prepared through salt metathesis between $InCl_3$ and K_2(salfen) followed by treating (salfen)InCl with $KOtBu$,[38] while late transition metal complexes such as M(salfen) (M = Co, Zn) were also prepared by salt metathesis from the corresponding metal chlorides.[87]

Scheme 2: Synthesis of rare-earth metal complexes supported by (a) NN^{fc} (using NN^{TBS} as an example) and (b) OEEO^{fc} (using salfen and phosfen as examples) ligands.

C. C-H Activation, Dearomatization, and Ring-Opening Reactions of aromatic N-heterocycles
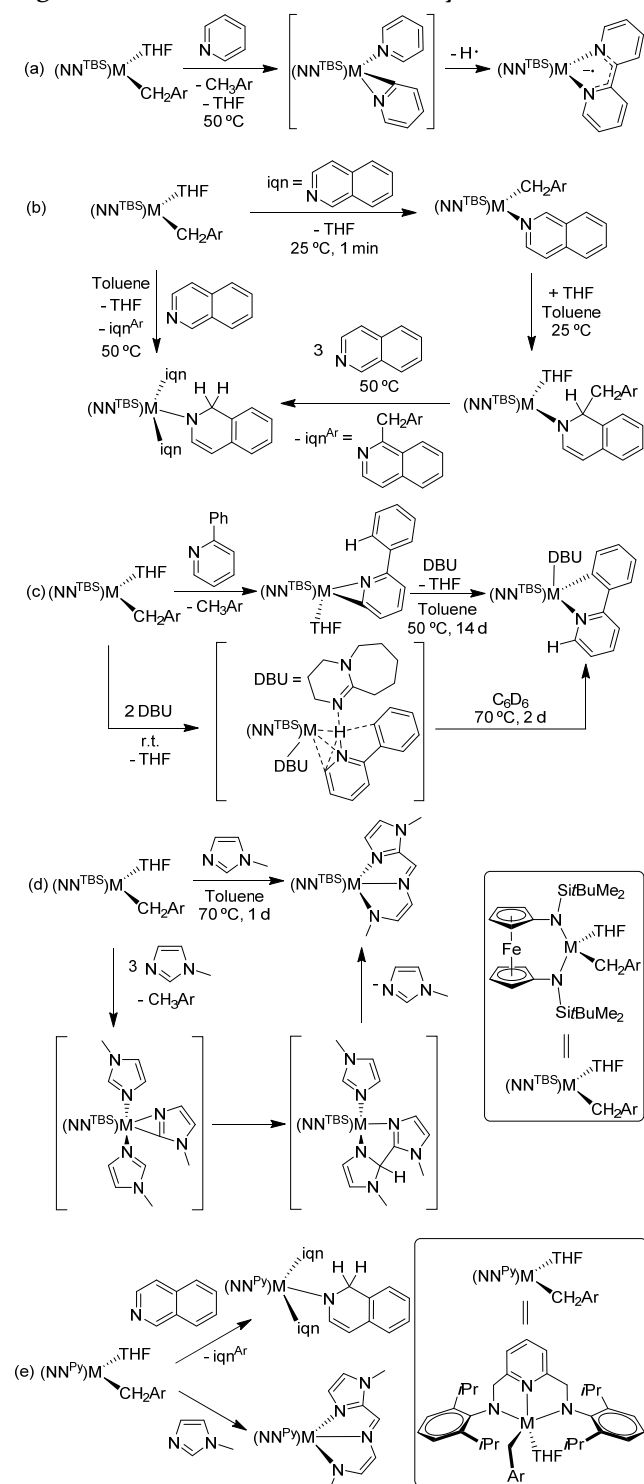
Scheme 3: Reactivity of rare-earth metal alkyl complexes supported by ferrocene diamide ligands toward aromatic N-heterocycles: (a) C-H activation of pyridine followed by C-C coupling and formation of bipyridine radical anion;[63] (b) dearomatization of isoquinoline;[65] (c) C-H activation of 2-phenylpyridine followed by hydrogen migration;[54] (d) ring-opening of 1-methylimidazole;[82] (e) reactivity of pincer-type pyridine diamide complexes.[67]

Rare-earth metals are highly electropositive and can activate strong C-H bonds typically through a σ-bond metathesis mechanism. Since the seminal report by Watson on the methane exchange reaction at Cp*$_2$LuMe,[100] rare-earth metal complexes have been widely studied for the activation of aromatic C-H bonds.[101-103] Our group has focused on the reactivity of $(NN^{fc})M(CH_2Ar)(THF)_x$ with aromatic N-heterocycles in order to develop hydrodenitrogenation methods to remove nitrogen-containing impurities in fossil fuels.[104] The details of this reactivity were summarized in previous reviews,[72, 80] and, therefore, herein only the role of the ferrocene backbone in promoting unique reactivity will be discussed.

Rare-earth metal alkyl complexes supported by the NN^{TBS} ligand react with a wide range of aromatic N-heterocycles, including pyridine (Scheme 3a), isoquinoline (Scheme 3b), 2-phenylpyridine (Scheme 3c), and 1-methylimidazole (Scheme 3d). The reactivity varies depending on the substrate: C-H activation and alkyl transfer are the most common first steps of activation followed by subsequent C-C coupling, hydrogen transfer, or in some cases, ring opening of heterocycles. In most rare-earth metal alkyl complexes, the iron-metal distance is close to the sum of covalent radii thus indicating a donor-acceptor interaction of moderate strength.[72]

We also synthesized rare-earth metal alkyl complexes supported by a pincer-type pyridine-diamide ligand (NN^{Py}, Scheme 3) and studied their reactivity toward aromatic N-heterocycles. We observed that they showed similar reactivity as rare-earth metal alkyl complexes supported by ferrocene diamide ligands (Scheme 3e).[67] This result indicated that ferrocene diamide ligands behaved similarly to the tridentate pincer ligand that features a strong metal-nitrogen interaction in a linear fashion, while the weak iron-metal interaction shields one side of the metal coordination sphere. The robustness of the ferrocene diamide ligand, however, allowed the observation and/or isolation of reactive intermediates and thus uncovered the step-by-step mechanisms of aromatic N-heterocycle activation that would otherwise be elusive.[65, 72, 77, 82]

Regarding the iron-metal interaction, we observed the following trend: the more electron-deficient the metal center the shorter the distance. A comparison of a series of scandium complexes supported by NN^{TBS} is shown in Chart 2. The sum of covalent radii of 3.02 Å[105] could be used as a measure to determine qualitatively the strength of the Fe-Sc interaction in those complexes. When a strong Lewis donor such as THF is coordinated to scandium, the Fe-Sc distance is long indicating a minimal interaction; when no such donors are present, like in the case of $[(NN^{TBS})Sc(\mu-Cl)]_2$, a rather short Fe-Sc distance was observed suggesting the presence of a significant donor-acceptor type interaction.[81] An interesting case is the dinuclear hydride complex $[(NN^{TBS})Sc(\mu-H)][(NN^{TBS})Sc(THF)(\mu-H)]$: one of the scandium ions has a coordinating THF molecule while the other does not. The corresponding Fe-Sc distances differed by 0.48 Å, with the short distance close to that of $[(NN^{TBS})Sc(\mu-Cl)]_2$ and the long distance close to that of $(NN^{TBS})ScMe(THF)_2$.[44] Despite the fact that the Fe-Sc bond

energy is estimated to be less than 10 kcal/mol and is much weaker than a typical chemical bond, the relatively large change in the Fe-Sc distance has a huge impact on the geometry of metal complexes, especially on the shielding effect of the ferrocene backbone. This is best illustrated in the extreme case of a scandium methylidene complex: heating the ring-opening product of 1-methylimidazole by a scandium alkyl complex in the presence of trimethylaluminum resulted in the isolation of a scandium methylidene complex.[58] Besides the Lewis acid supported scandium-

methylidene interaction, the most noticeable feature of this compound is the extreme short Fe-Sc distance of 2.66 Å, 0.36 Å shorter than the sum of covalent radii. The presence of a strong Fe-Sc interaction was also supported by DFT calculations: the calculated Mayer Fe-Sc bond order is 0.46; for comparison, the calculated bond order for Sc-N in the same complex is 0.41. The ferrocene backbone arguable played an important role in stabilizing the scandium methylidene complex.[58]
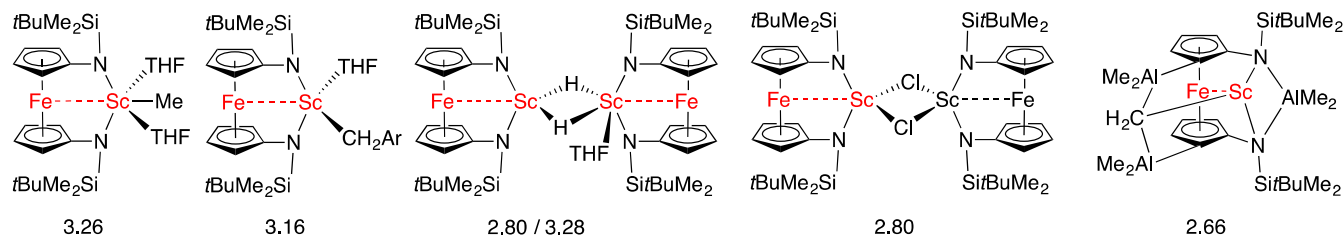

Chart 2. Iron-scandium distances (unit in Å) for selected scandium complexes[44, 58, 81] supported by the ferrocene diamide ligand NN^{TBS} (sum of covalent radii 3.02 Å[105]).

D. Reduction Chemistry with π Ligands and Small Molecule Activation

Rare-earth metals have long been considered redox-inert since most of them have only one stable oxidation state, +3.[106] However, chemists never stopped pushing synthetic limits and, recently, low valent lanthanide chemistry has emerged as a fast developing field.[107-109] Recent advancements feature the synthesis and characterization of divalent lanthanide complexes for the complete lanthanide series,[110-116] reduced dinitrogen complexes,[117-121] reduced arene complexes,[26-29, 57, 122-126] and bimetallic reductive cleavage of aromatic C-H bonds.[40, 44] Our group focused on the reduction chemistry of rare-earth metal complexes with non-innocent π ligands, followed by a small molecule activation study.[47, 51] Much of the work was summarized in previous reviews.[27, 28, 40] Herein, we are going to highlight the role of the ferrocene ligand in stabilizing unusual moieties and promoting unprecedented reactivity.

We were able to synthesize a series of inverse sandwich metal arene or alkene metal complexes, such as naphthalene, anthracene,[57] biphenyl, p-terphenyl, 1,3,5-triphenylbenzene,[29] and (E)-stilbene[45] with a general formula $[(NN^{TBS})M(THF)_x]_2(\mu\text{-arene})[K(solvent)]_y$ (for arene = naphthalene, anthracene, and (E)-stilbene, y = 0, x = 0 for M = Sc or x = 1 for other rare-earth metals; for arene = biphenyl, p-terphenyl, 1,3,5-triphenylbenzene, y = 2 and x = 0). For the doubly reduced arene in $[(NN^{TBS})M(THF)_x]_2(\mu\text{-arene})$, the negative charges were delocalized over two or more phenyl rings and thus the metal ions coordinated to different rings, in agreement with an ionic interaction with the rare-earth metal.[57] However, for the quadruply reduced arenes in $[(NN^{TBS})M]_2(\mu\text{-arene})[K(solvent)]_2$, the negative charges were mainly localized on one phenyl ring with the

metal ions coordinated to opposite sides of the same ring. The localization of negative charges was rationalized to be the result of the aromatic stabilization energy of a 6C, 10π-electron system. The rare-earth metal ions also played an important role in the stabilization of the quadruply reduced benzene tetraanion as DFT calculations revealed a covalent interaction between the metal orbitals and the π* orbitals of benzene with δ symmetry.[29, 39] The Fe-M distance varies for different compounds. For $[(NN^{TBS})Sc]_2(\mu\text{-}C_{10}H_8)$, the Fe-Sc distance was 2.83 Å, 0.19 Å shorter than the sum of covalent radii; for $[(NN^{TBS})Y]_2(\mu\text{-}C_6H_5Ph)[K(toluene)]_2$, the Fe-Y distance was 3.22 Å, same as the sum of covalent radii (Scheme 4). The difference in the ferrocene-metal interaction likely reflects the change of metal-arene interaction (from ionic in the doubly reduced arene complex to a strong covalent interaction in the quadruply reduced arene complex). We deem that the capacity of the ferrocene diamide ligand to have a flexible coordination mode is essential for the stabilization of rare-earth complexes featuring various π ligands. The divergent reactivity of rare-earth metal naphthalene complexes with P_4 is a good example: while $[(NN^{TBS})Y(THF)]_2(\mu\text{-}C_{10}H_8)$, with a weaker Fe-Y interaction (distance of 3.21 Å, sum of covalent radii of 3.22 Å), led exclusively to $[(NN^{TBS})Y(THF)]_3P_7$, $[(NN^{TBS})Sc]_2(\mu\text{-}C_{10}H_8)$, with a stronger Fe-Sc interaction (distance of 2.83 Å, sum of covalent radii of 3.02 Å), yielded two products, $[(NN^{TBS})Sc]_3P_7$ and $[(NN^{TBS})Sc]_4P_8$ (Scheme 4). We hypothesized that the tighter binding between the ferrocene backbone and scandium provided an additional protection around the scandium center and thus allowed the formation of a unique realgar-type P_8 tetraanion.[51]
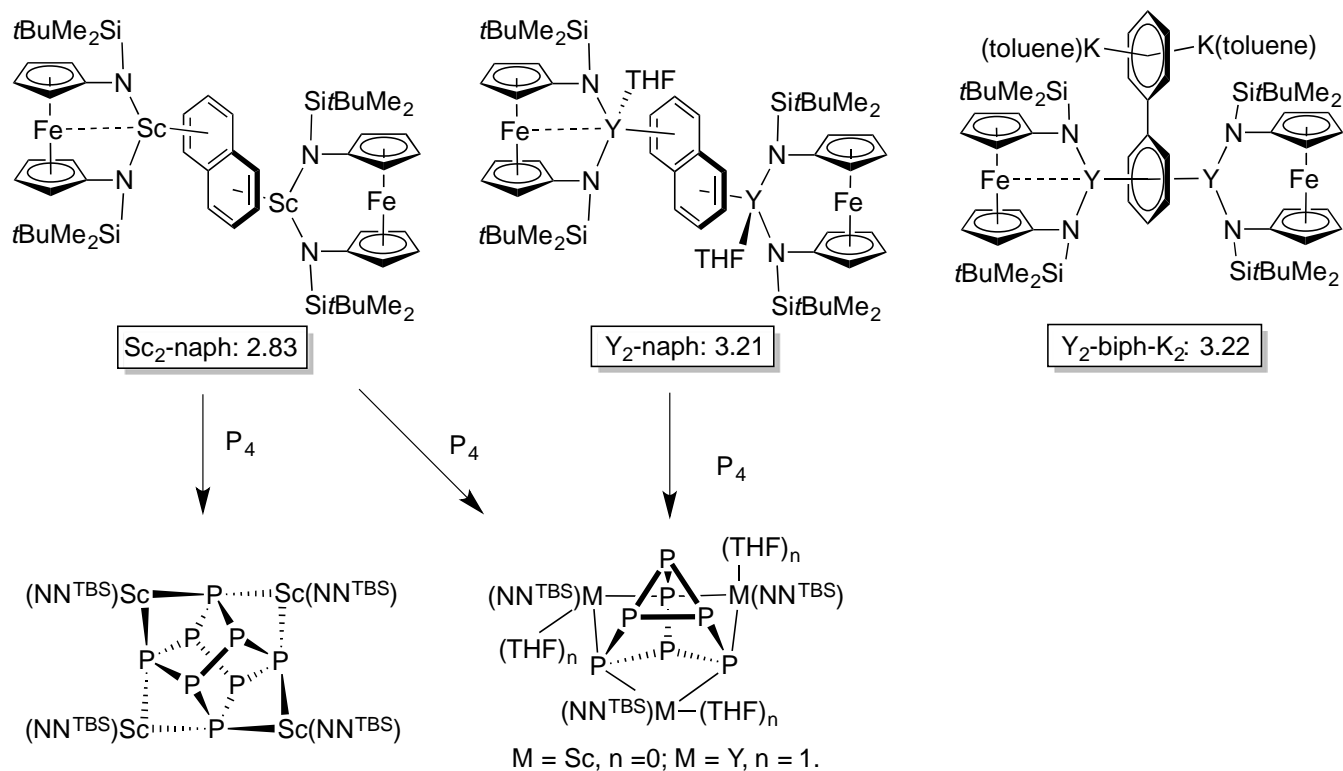
Scheme 4: Rare-earth metal arene complexes featured by the type of Fe-M interaction and divergent reactivity for P_4 activation.

In our pursuit of synthesizing a rare-earth metal reduced benzene complex, we discovered a new type of C-H bond activation, bimetallic reductive cleavage of aromatic C-H bonds.[44] Reacting $(NN^{TBS})ScI(THF)_2$ and KC_8 in benzene resulted in the equimolar formation of a scandium hydride $[(NN^{TBS})Sc(\mu-H)]_2$ and a scandium phenyl $(NN^{TBS})ScPh(THF)$ product. A mechanistic study was consistent with a proposed benzene dianionic intermediate (Figure 1). DFT calculations revealed interesting facts about the iron-metal interaction throughout the proposed reaction pathway. In the asymmetric benzene dianionic intermediate, the Fe-Sc distances were 3.10 and 3.04 Å for the η^6-bound and η^3-bound $(NN^{TBS})Sc$ fragment, respectively. The longer Fe-Sc distance indicated a minimal bonding interaction between iron and scandium.

While the Fe-Sc distance for one $(NN^{TBS})Sc$ fragment only slightly decreased in the transition state from 3.04 Å to 2.99 Å, the other Fe-Sc distance significantly shortened from 3.10 Å to 2.90 Å, a change of 0.20 Å (Figure 1). This sharp change was accompanied by a change in the scandium coordination environment: in the benzene dianionic intermediate, the scandium ion is η^6-bound to the π face of benzene, making it electron-sufficient and coordinatively saturated; however, in the transition state, the same scandium ion is σ bound to the *ipso*-carbon atom and partially bound to the hydrogen of the to-be-broken C-H bond, making it electron-deficient and coordinatively unsaturated. The strengthening of the Fe-Sc interaction in the transition state compensates for the loss of electron density and coordination saturation and, therefore, should lower the energy barrier for C-H bond cleavage. On the contrary, the other scandium, which keeps η^3-bound to the benzene dianionic ligand, experienced only a minimal structural change in the transition state, in general, and a small change of the Fe-Sc distance, in particular. Finally, in the product, both Fe-Sc distances elongated significantly to 3.10 and 3.39 Å upon the formation of the mixed bridging phenyl and hydride product. This result highlights the important role of the ferrocene backbone in promoting this new C-H bond activation reactivity: the flexible coordinating ability allows it to act when needed; in turn, this lowers the energy barrier for the transition state without the need for interfering external reactants, intermediates, and products.
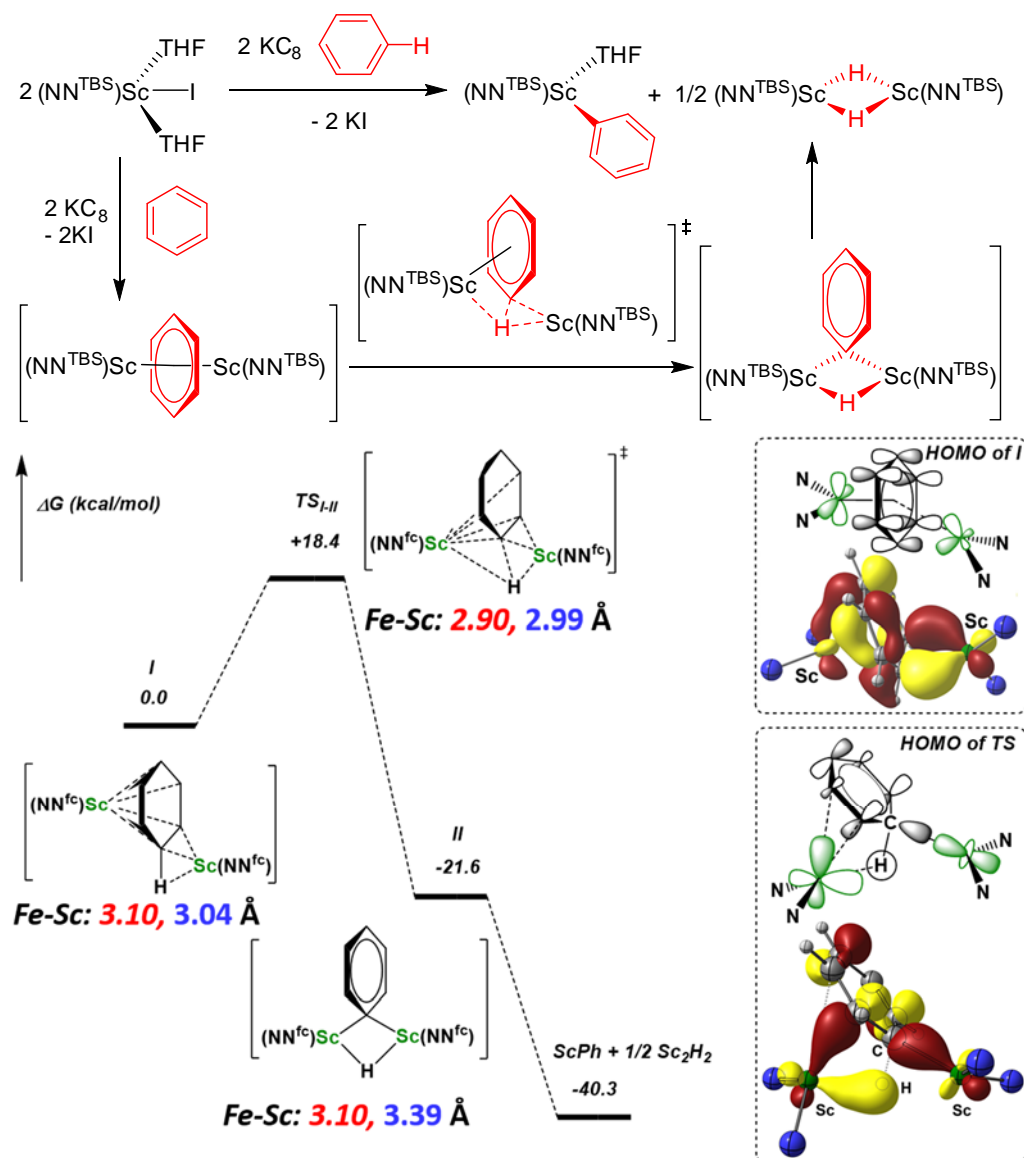
Figure 1: Top: proposed mechanism for the bimetallic reductive cleavage of aromatic C-H bonds; bottom: calculated reaction coordinates highlighting the role of the ferrocene backbone by indicating Fe-Sc distances for both ferrocene fragments.

E. Redox-Switchable Catalysis Enabled by Redox Active Metals or Ligands

As we stated in the introduction, ferrocene-based ligands inherit a reversible redox character from their ferrocene backbone.[127] Redox control at ligands containing ferrocene or its derivatives has been realized to influence the reactivity of the catalysts.[128, 129] Therefore, rare-earth metal alkoxide complexes supported by salfen and phosfen ligands were synthesized since these metals are known to catalyze the ring-opening polymerization of cyclic esters with high reactivity.[78, 130-135] We first synthesized yttrium(III) and cerium(IV) complexes, (salfen)Y(OtBu)(THF) and (salfen)Ce(OtBu)$_2$, supported by the Schiff base salfen ligand (H$_2$(salfen) = 1,1'-di(2,4-di-$tert$-butyl-salicylimino)ferrocene).[78] However, although both Y(III) and Ce(IV) complexes can serve as good catalysts for lactide polymerization, attempts to oxidize the ferrocene backbone using ferrocenium salts were not successful. An electrochemical study of those complexes using cyclic voltammetry revealed that the Fe$^{2+/3+}$ redox potentials for H$_2$(salfen) and the corresponding yttrium complex (salfen)Y(OtBu)(THF) were more positive than that of Cp$_2$Fe$^{0/+}$, while that of the cerium(IV) complex (salfen)Ce(OtBu)$_2$ was close to Cp$_2$Fe$^{0/+}$. However, when turning to other oxidants such as a brominated triphenylamine radical or silver triflate, the reaction was not clean and thus not appropriate for redox-controlled catalysis.[78] The issue was solved by the introduction of a new ligand, phosfen (H$_2$(phosfen) = 1,1'-di(2-$tert$-butyl-6-diphenylphosphiniminophenol)ferrocene). H$_2$(phosfen) could be readily synthesized from fc(N$_3$) and a substituted phosphine. The cyclic voltammetry of H$_2$(phosfen) and the corresponding Y(III) and Ce(IV) complexes (phosfen)Y(OtBu) and (phosfen)Ce(OtBu)$_2$ showed a reversible redox event at a more negative potential compared to the corresponding salfen analogues.[59] This allowed the use of a soluble oxidant, [Cp$_2$Fe]$^+$[BAr$^F_4$] (Ar^F =

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3,5-$(CF_3)_2C_6H_3$), and a soluble reductant, Cp_2Co, to oxidize/reduce (phosfen)Y(OtBu)(THF) and (phosfen)Ce(OtBu)$_2$ reversibly and instantaneously at room temperature. For lactide polymerization, the oxidized species, [(phosfen)Y(OtBu)]$^+$[BAr$^F_4$]$^-$, was not active (Figure 2).
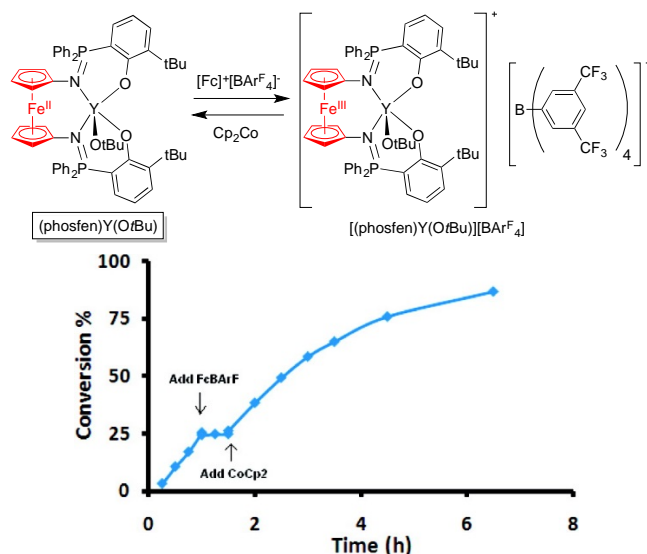
Figure 2: Redox controlled lactide polymerization at a remote ferrocene ligand site of a rare-earth metal catalyst.

Therefore, we achieved control of lactide polymerization by chemically oxidizing or reducing the catalyst at a remote site of catalysis, the ferrocene backbone of the phosfen ligand (Figure 2).[61] The difference in reactivity between the oxidized and reduced forms of the catalyst was attributed to changes in their electronic profiles. We hypothesized that the oxidized ferrocenium ligand would make the rare-earth metal center so electron deficient that once the substrate binds to the metal it cannot leave, thus interrupting the catalytic cycle.

Notably, for the cerium(III) phosfen complex (phosfen)Ce(OtBu)(THF), there were two oxidation events: the first was assigned to the Ce$^{3+/4+}$ redox couple at a far more negative potential compared to Fe$^{2+/3+}$. By taking advantage of the Ce(III)/Ce(IV) switch, we were also able to achieve a similar control of lactide polymerization directly at the metal site.[60] Recently, we applied this strategy to other electropositive metals including indium,[38] titanium, and zirconium.[43] In case of group 4 metals, by using (thiolfan)Zr(OtBu)$_2$ and (thiolfan*)Ti(OiPr)$_2$ as the reduced form of catalysts, we were able for the first time to achieve orthogonal reactivity through redox control of a remote site of the supporting ligand: the reduced form of the catalyst catalyzed lactide but not ε-caprolactone polymerization, while the opposite was true for the oxidized form of the catalyst. Because of the robustness of the ferrocene-based ligand, we anticipate that this redox-switchable strategy could be general and may be applied to make valuable co-polymers in a more efficient way than current state-of-the-art methods.
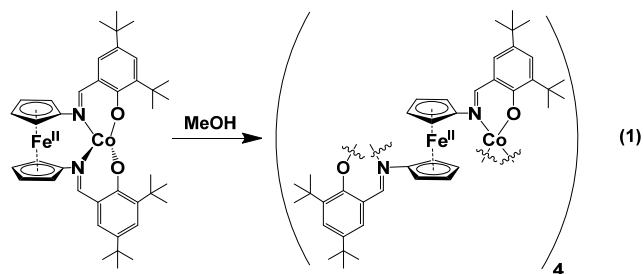
The ligand flexibility proved also important in realizing redox switchable hydroalkoxylation of styrene derivatives.[136] The hydroalkoxylation reaction was proposed to involve the formation of a cobalt hydride. In order to access this catalytically active species, it was proposed that the precursor complex, Co(salfen) (salfen = 1,1'- di(2,4-di-*tert*-butyl-6-salicylimine)ferrocene), must exhibit some fluxional behavior in solution to open up a coordination site necessary for the hydride ligand. The possibility of this fluxional behavior was evidenced by the formation, in the presence of methanol (Eq 1), of a tetrameric structure, in which the two phenolate arms of each ferrocene are coordinated to two different cobalt centers.

Summary

Ligands play an ever-increasing role in organometallic chemistry, in general, and metal catalyzed transformations, in particular. With the advancement of fundamental inorganic and organometallic chemistry, a deep understanding of how a supporting ligand cooperates with a metal in promoting bond breaking and formation is possible. As a result, the rational design of a ligand is possible and underway not only to fit the size and oxidation state of a metal but also to enhance its reactivity or empower unprecedented transformations. Our journey in exploring ferrocene-based ligands in rare-earth and transition metal chemistry is a showcase of that concept. Currently, we are exploiting the rich chemistry enabled by flexible and redox non-innocent ferrocene-based ligands for rare-earth metals, actinides, and other metals including late transition metals in order to study further unusual transformations and applications to material synthesis.[42, 48, 53, 87]

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For Table of Contents Only: The introduction of ferrocene-based ligands into organolanthanide chemistry not only helped to study intriguing fundamental problems but also led to fruitful chemistry including small molecule activation and controlled co-polymerization.