

## PN3(P)-Pincer Complexes: Cooperative Catalysis and Beyond

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# PN<sup>3</sup>(P)-Pincer Complexes: Cooperative Catalysis and Beyond

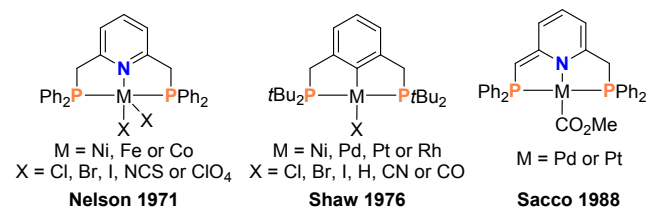
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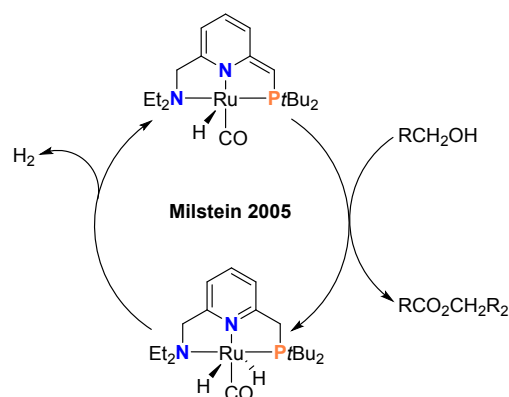
KEYWORDS: PN<sup>3</sup>(P)-pincer, Catalysis, Metal–ligand cooperation, pseudo-aromaticity

## 1. INTRODUCTION

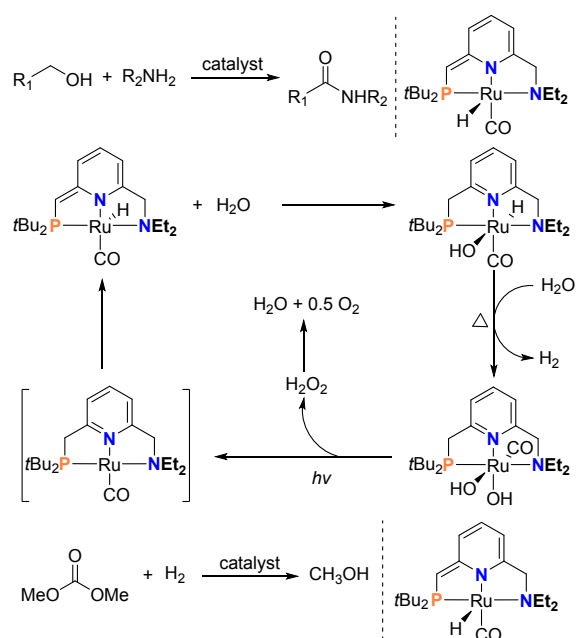
Organometallic catalysis takes advantage of the ability to introduce highly distinctive reactivity of the corresponding metal complexes by modifying the ligand steric and electronic properties. The tridentate pincer ligands, that enforce the meridional coordination around the metal center upon complexation, have become a powerful platform in catalyst design because of the enhanced stability and flexibility for synthetic modifications.<sup>1</sup> Considerable progress has been made in the pincer chemistry after the pioneering reports in the 1970s by Nelson and the Shaw groups (Scheme 1).<sup>1,2</sup> Among them, the pyridine-based pincer complexes are particularly attractive. The studies on the synthesis and application of numerous categories of so-called PNP (or PNN) pincer complexes started from the first examples in 1971.<sup>2a</sup> While the deprotonation of one of the CH<sub>2</sub> arms was observed in the synthesis of PNP palladium and platinum complexes by Sacco *et al.*,<sup>3</sup> it was not until 2005 when a remarkable discovery of a new mode of metal–ligand cooperation (MLC) involving dearomatization/rearomatization processes of pyridine-based pincer complexes was made by Milstein and co-workers (Scheme 2).<sup>4</sup> This represents an important milestone in the historical development of catalytic applications of pyridine-based pincer complexes<sup>5</sup> and such a unique MLC involving ligand aromatization–dearomatization processes enables facile activation of various chemical bonds and environmentally benign catalysis.<sup>5</sup> Soon enough, this concept was further applied in several extraordinary reactions by the Milstein group: the dehydrogenative acylation of amines with alcohols,<sup>6</sup> water splitting,<sup>7</sup> hydrogenation of carbonates,<sup>8</sup> *etc.* (Scheme 3).



Scheme 1. PNP and PCP pincer complexes.



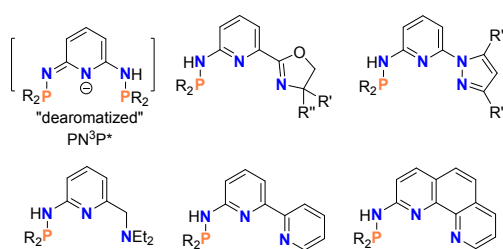
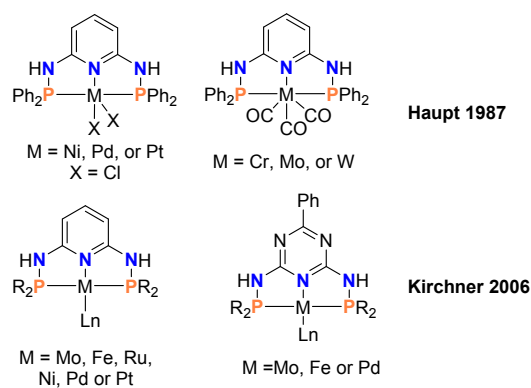
Scheme 2. The discovery of a dearomatized pincer Ru complex as an effective catalyst.



Scheme 3. Selected examples of MLC catalysis developed by the Milstein group.

**Table 1.** Differences in bond-dissociation energies (BDEs) between C–H and N–H bonds.

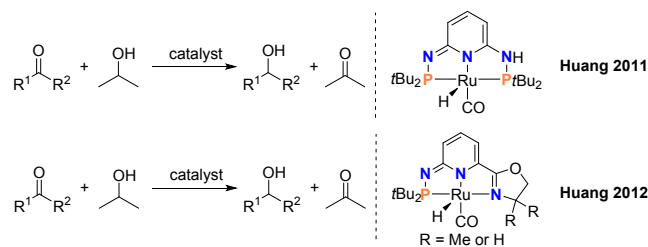
	H <sub>2</sub> N–H	PhNH–H	Ph <sub>2</sub> N–H
BDE (kcal/mol):	107	92	87.5
	H <sub>3</sub> C–H	PhCH <sub>2</sub> –H	Ph <sub>2</sub> CH–H
BDE (kcal/mol):	105	88	82

**Scheme 4.** The PN<sup>3</sup>(P)-pincer ligand platform designed by the Huang group.**Scheme 5.** Earlier studies on the coordination chemistry of PN<sup>3</sup>P-pincer complexes.

Inspired by the Milstein mode of substrate activation and also recognizing the distinct properties of N–H bonds as they are more acidic and yet stronger than C–H ones (Table 1), we started the investigation on the potential MLC reactivities by replacing the CH<sub>2</sub> arms with one or two NH groups, with the idea that the more acidic N–H bond can facilitate the deprotonation (and thus dearomatization) process while the reprotonation/rearomatization process may allow different bond activation and formation events due to the stronger N–H bonds. Accordingly, we have designed and synthesized a series of symmetrical and unsymmetrical pincer ligands and the corresponding metal complexes (Scheme 4).<sup>9</sup> The term “PN<sup>3</sup>(P)” was proposed by us in an invited review to denote this class of ligands since “N” can be either a spacer or a coordinating atom.<sup>9,10</sup> In fact, the synthesis of symmetric PN<sup>3</sup>P pincer complexes based on 2,6-diaminopyridine were first reported by Haupt and co-workers in 1987,<sup>11</sup> and a simple and modular synthetic strategy for various PN<sup>3</sup>P pincer ligands was also developed by Kirchner and co-workers in 2006 (Scheme 5).<sup>12</sup> While the coordination chemistry and catalytic applications of these symmetric PN<sup>3</sup>P pincer

complexes have been intensively studied for 24 years,<sup>13</sup> the catalytic applications involving deprotonation/reprotonation of the NH arm and dearomatization/rearomatization of the central pyridine ring were unknown until our discovery in 2011 (Scheme 6).

<sup>9,14</sup>

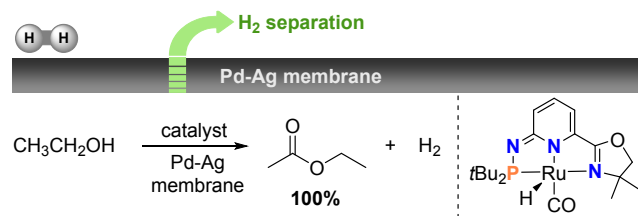
**Scheme 6.** Catalytic studies on the PN<sup>3</sup>(P)-pincer complexes involving MLC.

During the course of the exploring the effect of NH spacers in the backbone of PN<sup>3</sup>(P)-pincer complexes, we have immediately recognized that this seemingly small change from CH<sub>2</sub> to NH in the spacer of the ligand resulted in remarkably different kinetic and thermodynamic properties that in some cases enhanced or in more cases completely altered the catalytic activities due to the inherent features of this unique ligand platform.<sup>9b, 14b, 15, 16</sup> Based on the findings from us and others, the steady growth of PN<sup>3</sup>(P)-pincer chemistry have been seen.<sup>9b, 15d, 17</sup> Unfortunately, the deprotonation/reprotonation and dearomatization/rearomatization processes involving the NH arm in PN<sup>3</sup>(P)-pincer complexes as crucial steps have been largely neglected and overlooked in the mechanistic discussion and catalyst design in recent research articles<sup>17a, 17b, 17d–g, 17j–l</sup> and reviews.<sup>2d, 13b, 18</sup>

The aim of this Viewpoint is thus to familiarize the readers with the historical development, progress, and more importantly the distinct potential of the PN<sup>3</sup>(P)-pincer chemistry in the following three aspects: (i) reactivities of the PN<sup>3</sup>(P)-pincer complexes with special attention to the MLC via dearomatization/rearomatization; (ii) rationale for the kinetic and thermodynamic differences caused by the replacement of the CH<sub>2</sub> spacers with NH groups in the PN<sup>3</sup>(P)-pincer platform; and (iii) concluding remarks for the future potential of the PN<sup>3</sup>(P)-pincer chemistry.

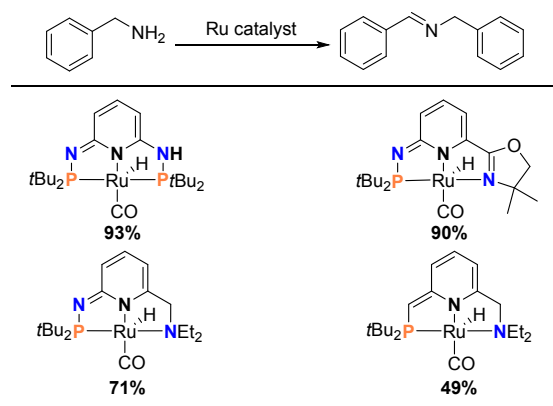
## 2. THE DISCOVERY OF THE PN<sup>3</sup>(P)-PINCER CHEMISTRY

Owing to the great success of the Milstein system,<sup>5a, 5c, 5d, 19</sup> we designed and prepared a series of PN<sup>3</sup>(P)-Ru complexes for comparison and demonstrated that the “dearomatization” could be achieved through the deprotonation of the N–H group.<sup>14</sup> Very interestingly, while Milstein’s PNN complex showed unprecedented activity towards water splitting,<sup>7</sup> ours were stable in the presence of water even under heating at above 80 °C overnight!<sup>4</sup> Significant thermodynamic differences between the two systems were evidenced. In fact, our early preliminary calculations also



**Figure 1.** Quantitative conversion of ethanol to ethyl acetate and hydrogen.

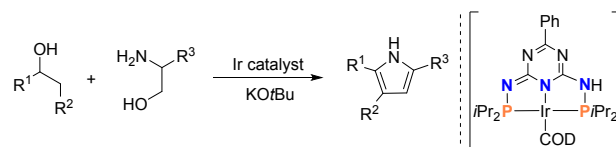
revealed that the addition of water or H<sub>2</sub> molecules to our dearomatized species were thermodynamically uphill. However, the energy differences between those of the computed complexes after the addition reaction and those of dearomatized species were small (2-5 kcal/mol),<sup>9b</sup> suggesting that these potentially catalytically active intermediates were still thermodynamically accessible. Indeed, at slightly more elevated temperatures (160 °C), our dearomatized PN<sup>3</sup>(P)\*-Ru complexes were active in hydrogen transfer reactions, dehydrogenation and hydrogenation reactions.<sup>14b, 15a, 15b, 15d, 15f, 15g, 15j, 15p, 15r, 15s, 15u, 16</sup> More importantly, such an enhanced thermostability (thus a higher reaction temperature is needed) became advantageous for us to integrate with the design of a palladium-based membrane reactor that can only work efficiently and effectively at high temperatures. Accordingly, in collaboration with the Lai group, the first demonstration of quantitative conversion of bio-renewable ethanol to the industrially important solvent and starting material, ethyl acetate, was achieved with H<sub>2</sub> as a valuable byproduct (Figure 1).<sup>15b</sup>



**Figure 2.** Coupling of amines to imines under oxidant-free conditions.

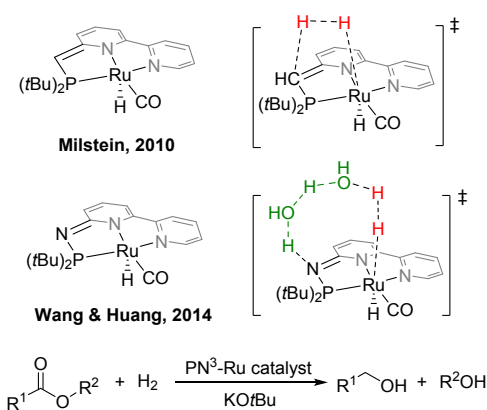
The dehydrogenative coupling of alcohols and amines to amides is one of the most impressive reactions invented with the MLC concept by Milstein.<sup>6</sup> Extremely interestingly, the dearomatized PN<sup>3</sup>(P)\*-Ru complexes gave very poor reactivities towards the amide formation although Hong and co-workers have shown that the same reactions could be achieved by simply mixing RuCl<sub>3</sub> salt and a carbene ligand precursor.<sup>20</sup> After careful analysis of the resulting products, it was found that the PN<sup>3</sup>(P)\*-Ru

complexes were more selective for the dehydrogenation of amines. In contrast, Milstein's catalyst exhibited a lower reactivity in the same reaction (Figure 2). A protocol for the coupling of amines to imines was thus developed.<sup>15a</sup> This was the time we realized that this seemingly small change from CH<sub>2</sub> to NH in the spacer of the ligand could lead to dramatic influences on the reactivities of the resulting transition metal complexes. We had then dedicated ourselves to the mechanistic understanding to enable the future development of new reactions with this distinct ligand platform.



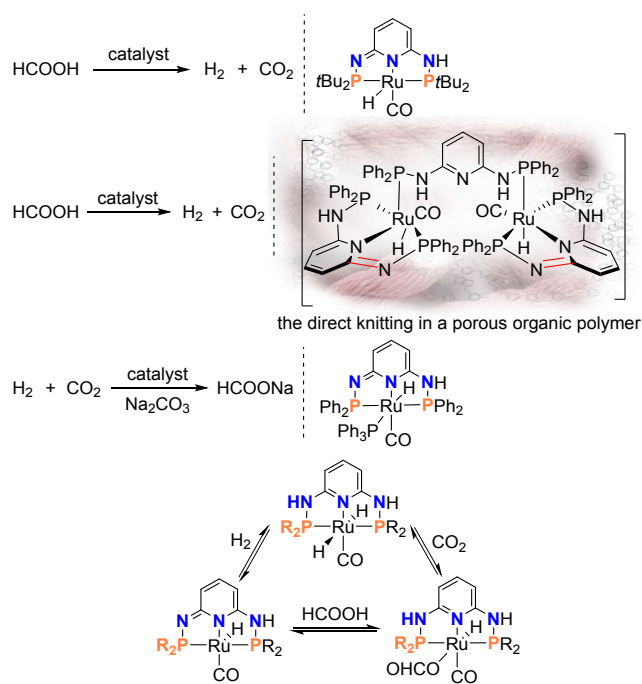
**Scheme 7.** Dehydrogenation reactions catalyzed by PN<sup>3</sup>P-Ir complexes.

During the course of our mechanistic investigations, Kempe and co-workers have reported the dehydrogenative coupling of secondary alcohols and β-amino alcohols to synthesize pyrroles catalyzed by PN<sup>3</sup>P-Ir complexes.<sup>17a</sup> In collaboration with the Wang group, our DFT calculations supported that the dearomatized Ir complex was most likely to be the active catalytic species in this reaction and the proton shuttle process played an important role (Scheme 7).<sup>15d</sup> Along this line, when compared to the Milstein's PNN-Ru system, we further demonstrated that two protonic molecules, e.g. water or alcohol, were needed for H<sub>2</sub> activation in our PN<sup>3</sup>\*-Ru system in order to connect the reactive sites of the N atom of the imine arm with the Ru metal center (Figure 3).<sup>16a</sup> Remarkably, the PN<sup>3</sup>\*-Ru complex can effectively catalyze the ester hydrogenation even in the presence of water. These observations not only indicate that the dearomatization/rearomatization process via deprotonation/reprotonation of the CH<sub>2</sub> or N-H spacer is an essential step in both PNP/PNN and PN<sup>3</sup>(P) catalytic systems, but also illustrate their distinct kinetic properties.



**Figure 3.** Comparison between the systems with CH<sub>2</sub> and HN arms.

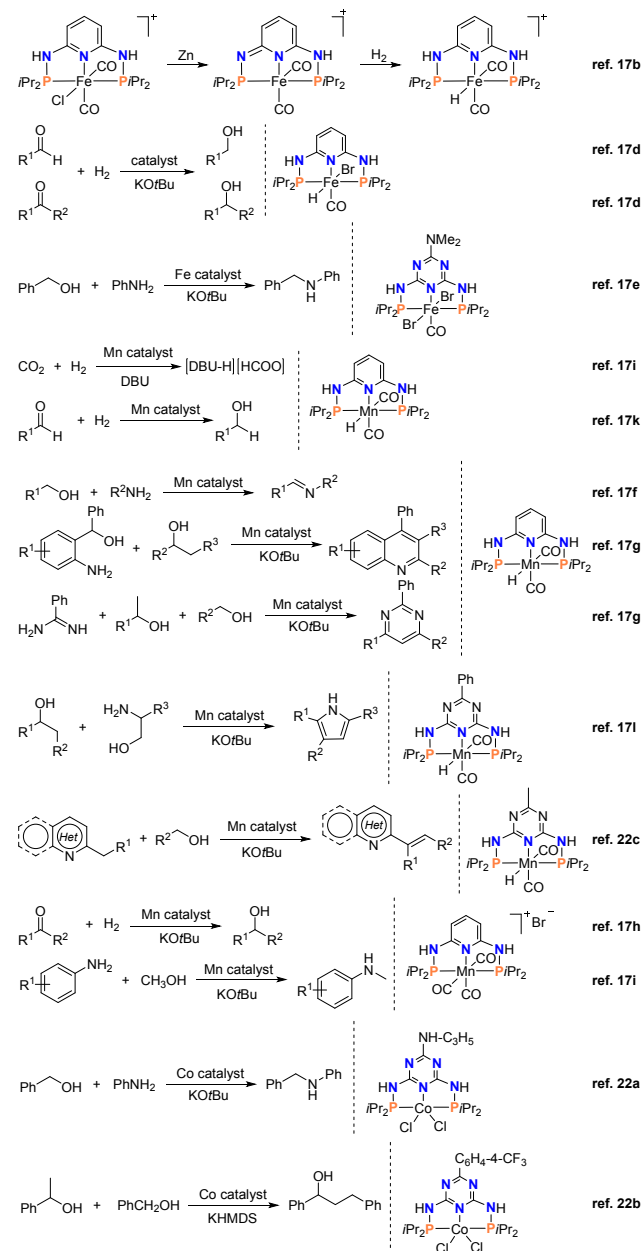
The enhanced stability in the presence of water is particularly important for the selective decomposition of formic acid to H<sub>2</sub> and CO<sub>2</sub> as a strategy to utilize formic acid as a hydrogen energy carrier.<sup>21</sup> In this regard, the PN<sup>3</sup>P\*-Ru complex showed excellent activity with an unprecedented long life.<sup>15b, 15u</sup> Notably, no decarbonylation reaction was detected, suggesting that a practical application is now possible. The conformation in solution of the transient formate intermediate in this process was recently elucidated by 2D-IR spectroscopy reiterating the important role of the N-H arm(s).<sup>15u</sup> Moreover, by replacing the *t*-butyl with phenyl groups, directly knitting the PN<sup>3</sup>P-Ru complex into a porous polymer network (featured with rigid methylene bridges using dimethoxymethane as an external crosslinker to combine the phenyl groups in the PN<sup>3</sup>P-Ru complex and benzene) resulted in a new porous heterogeneous ruthenium catalyst with single-atomic sites that offered a reusable catalyst with increased activity for the selective decomposition of formic acid (Scheme 8).<sup>15p</sup> Further studies on the reverse reaction revealed a good activity in the hydrogenation of CO<sub>2</sub> to formate. Remarkably, effective transformation of atmospheric CO<sub>2</sub> into formate was achieved in the presence of amines (Scheme 8).<sup>15r</sup>



**Scheme 8.** Formic acid decomposition and formation processes catalyzed by PN<sup>3</sup>P-Ru complexes via MLC.

The crucial role of the dearomatization/rearomatization via deprotonation/reprotonation of the NH arm in the PN<sup>3</sup>(P) pincer catalysis appears to be general. For example, Kirchner and co-workers described the heterolytic H<sub>2</sub> cleavage via the dearomatized PN<sup>3</sup>P-iron intermediate via MLC (Scheme 9).<sup>17b, 17d</sup> Catalytic alkylation of amines with alcohols was achieved but when NH groups were methylated to N-Me, the reactivity was shut down,<sup>17c</sup> suggesting the importance of the NH

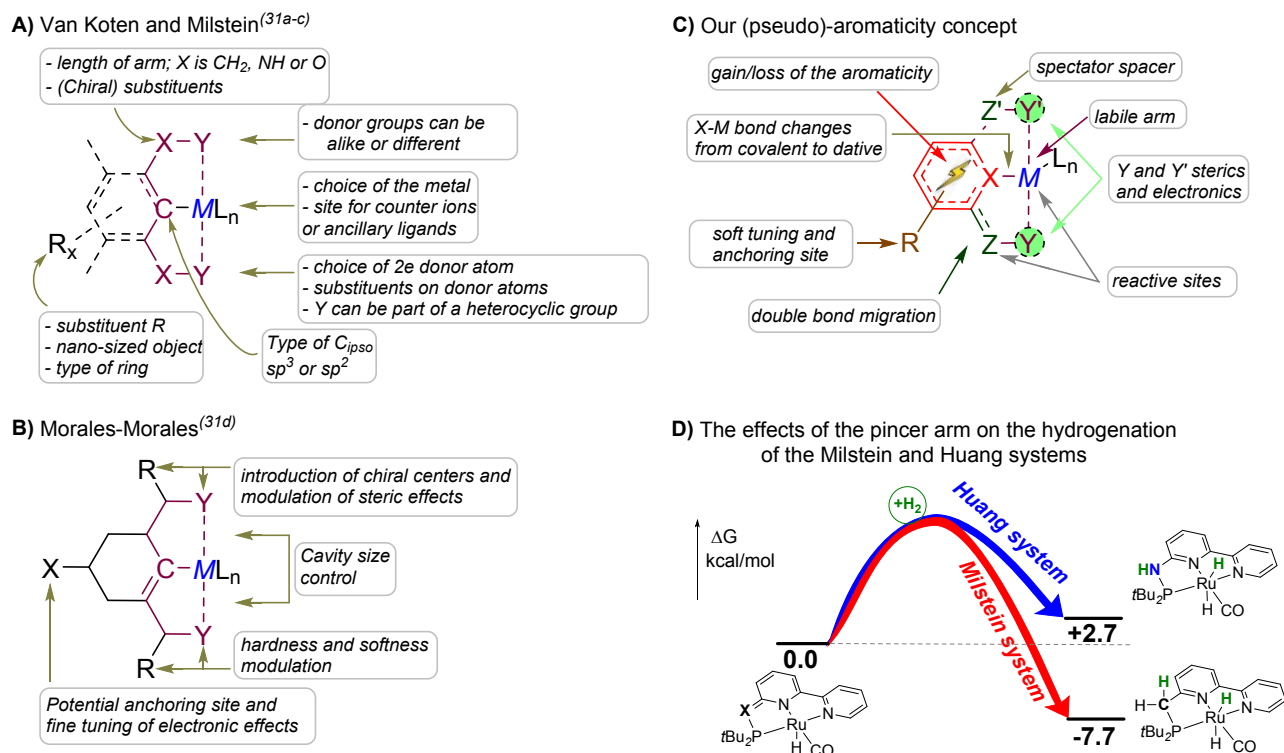
deprotonation/reprotonation process. Similar observations were also reported by the Sortais, Kirchner, and Kempe groups respectively in their Mn or Co analogs in various hydrogenative and dehydrogenative reactions (Scheme 9).<sup>17f-1, 22</sup>



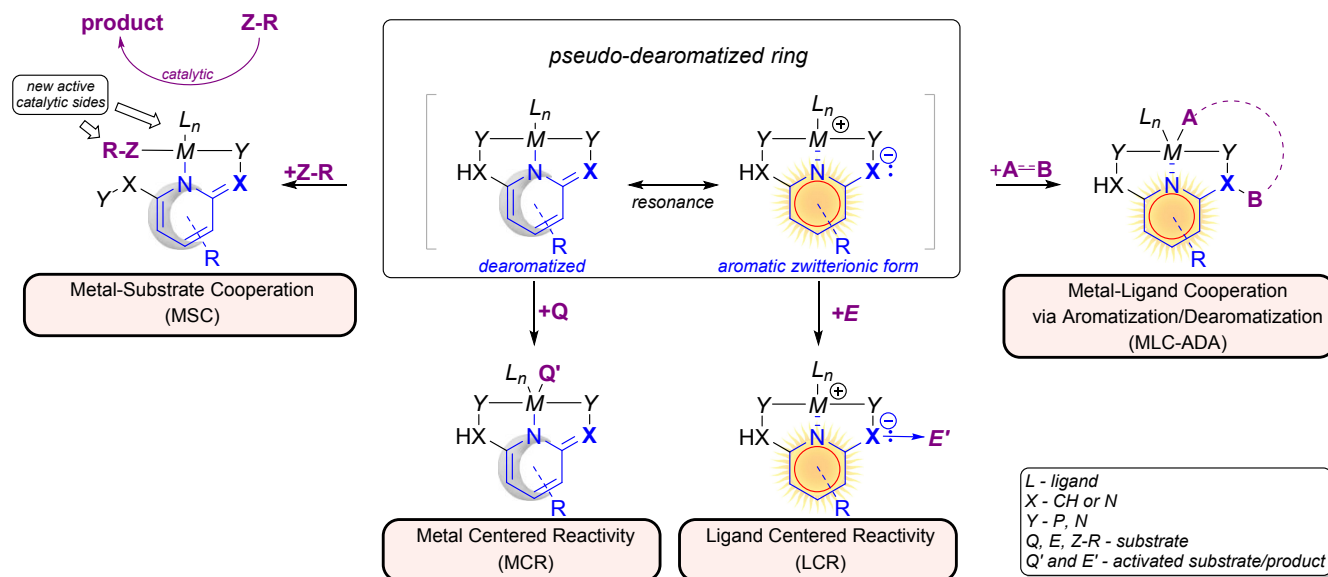
**Scheme 9.** MLC-triggered hydrogenation and dehydrogenation reactions catalyzed by PN<sup>3</sup>P-pincer complexes.

### 3. UNIQUE REACTIVITY MODES OF PN<sup>3</sup>(P)-PINCER COMPLEXES

Since the discovery of the catalytic applications of the dearomatized PN<sup>3</sup>(P)\* metal complexes, many groups join



**Figure 4.** Reactivity view of the PN<sup>x</sup>(P)<sup>\*</sup> pincer complexes.



**Figure 5.** Pictorial view of the key catalytic activation modes of the PN<sup>x</sup>(P)<sup>\*</sup> dearomatized pincer complexes.

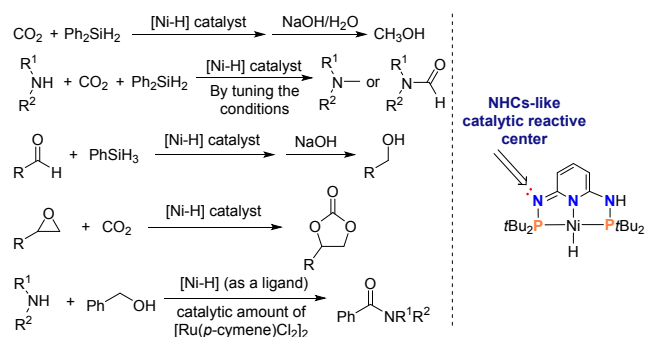
their efforts to understand and rationalize the reactivities of such systems for the small molecule activation,<sup>23</sup> dehydrogenative coupling,<sup>15d, 24</sup> and hydrogenation reactions;<sup>25</sup> under active debate. Li and Hall recently reviewed the reactions involving the pincer complexes and noted that aromatization/dearomatization step is not always the lowest energy path.<sup>26</sup> The Li and co-workers in

2009 suggested the importance of the hydrogen tunneling for the activation of the (PNP)IrPh complex,<sup>23b</sup> while Iron and co-workers proposed that the hydrogen transfer from ligand to metal was driven by aromatization in a heterolytic manner.<sup>23a</sup> Very recently, the study by Lei, Liu, Schaefer and co-workers introduced the metal-substrate mechanism rather than metal-ligand cooperation as a low

energy alternative pathway.<sup>27</sup> It was suggested that the proton shuttle mechanism is not involved in the lower energy pathway, which strongly contradicts with studies on other systems.<sup>23a, 23b, 28</sup> For some activation modes, the metal-ligand cooperation may occur without undergoing the aromatization/dearomatization step.<sup>29</sup> Collectively, the activation modes may be system sensitive, and molecular design can lead to unique chemical applications. The core of such diversity of reactivity modes lies on the cooperative properties and non-innocent character of the pyridine-based ligands.<sup>5, 9b, 30</sup>

As mentioned above, from the distinct frontier molecular orbitals of the imine and olefin arms in the dearomatized  $\text{PN}^x(\text{P})^*$  structures, we were able to rationalize the kinetic differences.<sup>15d, 16a</sup> In addition to the reactivity views suggested on the PCP ligands by van Koten, Milstein and Morales-Morales (Figures 4A and 4B)<sup>2d, 31</sup> and based on the our interest in the aromaticity,<sup>32</sup> we proposed the system based on the (pseudo)dearomatized platform (Figure 4C) and consequently elucidated the thermodynamic discrepancies between the Milstein and the Huang systems through different electron delocalization and aromatic stabilization energy (ASE) (Figure 4D).<sup>15k</sup> The “dearomatized”  $\text{PN}^3(\text{P})^*$  complexes indeed carry certain aromatic properties as the enhancement of ligand aromaticity through complexation becomes more pronounced compared to those of analogous dearomatized  $\text{PNP}^*$  or  $\text{PNN}^*$  based complexes, suggested by our nucleus-independent chemical shift (NICS<sub>zz</sub>), anisotropy of the current (induced) density (ACID), isochemical shielding surfaces (ICSS<sub>zz</sub>), and natural bond order (NBO) calculations.<sup>15k</sup> This work also represents the first example of theoretic studies on aromaticity in catalytic systems involving ligand dearomatization/rearomatization processes. More importantly, the view of the (pseudo)aromaticity has led to a novel paradigm of strategy for the catalyst design. The dearomatized pyridine-based  $\text{PN}^3(\text{P})^*$  pincer complexes must be understood by two leading resonance forms: neutral and zwitterionic structures (Figure 5).<sup>3, 15k</sup> The contribution of the aromatic form is much higher in the  $\text{PN}^3(\text{P})^*$  system than those in the  $\text{PNP}$  and  $\text{PNN}$  counterparts, partially from the difference of the atom electronegativity. In such flexible frame of pseudo-dearomatized frame, the metal center can act as an acid side and unsaturated arm can act as a basic side. As a result, the system expresses a few activation modes leading to unique reactivities incorporated in one system (Figure 5). The metal-centered reactivity (MCR) is conventional for the majority of metal complexes via ligand exchange, oxidative addition, reductive elimination, insertion, bond metathesis, *etc.*<sup>33</sup> The metal-substrate cooperation (MSC) was also suggested as the key step for some pincer complexes with labile arms.<sup>27</sup> In those two modes, the ligands do not participate in the catalytic reactions. The metal-ligand cooperation via aromatization/dearomatization (MLC-ADA) process requires unique rearrangement of the bonding patterns. In this transformation, two new sigma bonds are formed and the existing ones are rearranged to deliver the aromatic ring.<sup>15d, 15k</sup> Although MLC-ADA generally involves the metal

center and an unsaturated arm, it can also be promoted by metal and a reactive donor group.<sup>34</sup> The forth mode of the reactivity, ligand-centered reactivity (LCR), is highly intriguing and can be triggered by the non-innocent character of the ligand and/or enabled by the zwitterionic resonance characters.<sup>15t, 35</sup>



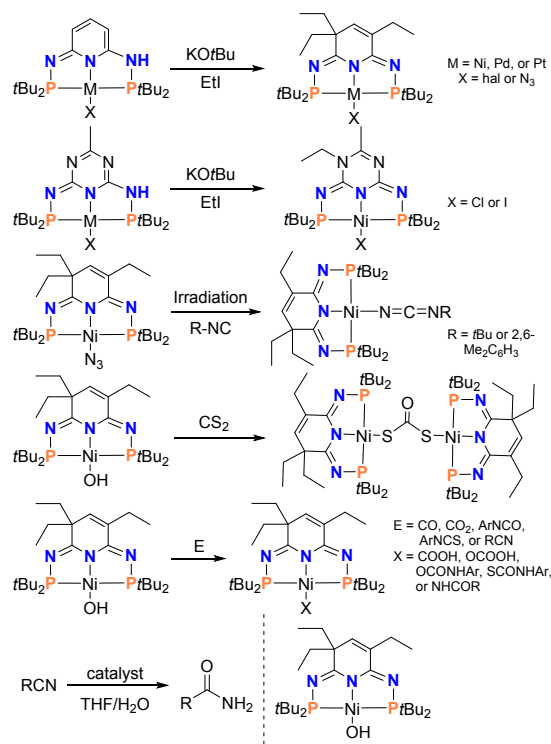
**Scheme 10.** A pseudo-dearomatized  $\text{PN}^3\text{P}^*\text{Ni-H}$  complex as a ligand and  $\sigma$ -nucleophilic catalyst.

For the  $\text{PNP}$  system, the basicity of the arm was studied experimentally by Milstein in 2010.<sup>36</sup> It was demonstrated that at ambient temperature the neutral form is entropically favored while the cationic form is favored in low temperature due to the effect of charge separation. In the  $\text{PN}^3\text{P}^*$  platform, the LCR offers unprecedented reactivities.<sup>15q</sup> The  $\sigma$ -nucleophilicity of the N atom of the iminic arm can be significantly enhanced such that it becomes catalytically active to reach N-heterocyclic carbene-like nucleophilicity in the hydrosilylation of  $\text{CO}_2$  to methanol, selective reductive methylation and formylation of amines with  $\text{CO}_2$ , hydrosilylation of aldehydes to alcohols, and cycloaddition of  $\text{CO}_2$  to epoxides, and serves as a ligand in the Ru-catalyzed dehydrogenative acylation of amines with alcohols (Scheme 10).<sup>15q, 15t</sup>

#### 4. COORDINATION CHEMISTRY BEYOND THE COOPERATIVE CATALYSIS

The structural modification in the pincer system can offer significantly different reactivities. Within the LCR concept, our initial progress in creating new ligand structures is encouraging.<sup>15l-o</sup> We have developed a post-modification strategy taking advantage of the enhanced ligand reactivity to prepare a new class of diimine-amido anionic  $\text{PN}^3\text{P}$ -pincer complexes, 2<sup>nd</sup> generation  $\text{PN}^3\text{P}$ , that could not be easily synthesized by conventional synthetic organic methods (Scheme 11). Upon treatment of dearomatized  $\text{PN}^3\text{P}$ -pincer complexes with excess amounts of a base (e.g.  $\text{KO}t\text{Bu}$ ) and an alkyl halide (e.g.  $\text{EtI}$ ), the backbone of the ligands can be alkylated. Unique activities were discovered. For example, the 2<sup>nd</sup> generation  $\text{PN}^3\text{P-Ni}$  azide complex can be photo-activated to react with isocyanides to afford monosubstituted carbodiimides, presumably via a transient nitrido intermediate.<sup>15m</sup> The 2<sup>nd</sup> generation  $\text{PN}^3\text{P-Ni}$  moiety allowed the isolation of a terminal hydroxide complex and enabled the investigation of the diverse

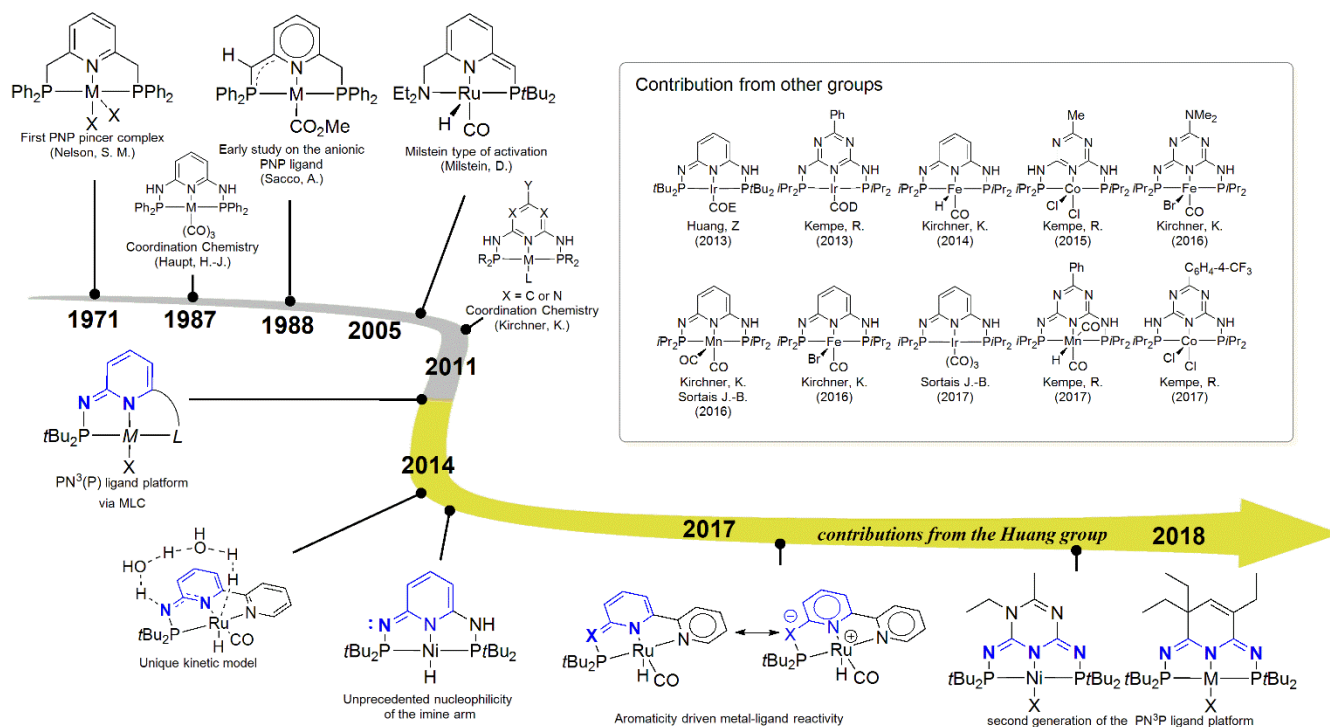
reactivities of the hydroxide group with respect to its nucleophilic



**Scheme 11.** Formation of a new PN<sup>3</sup>P-pincer platform through ligand post-modification and basic characters (Scheme 11).<sup>15n</sup> This monomeric Ni-OH complex was also identified to catalyze the nitrile hydration to various amides efficiently.

## 5. CONCLUDING REMARKS

PN<sup>3</sup>(P)-pincer complexes are not only incredibly effective catalysts for the hydrogenative and dehydrogenative reactions, but they also possess distinct kinetic and thermodynamic properties compared to their CH<sub>2</sub> analogs (i.e. the Milstein mode). We have elucidated the role of MLC and rationalized the influences of the aromaticity as crucial factors in the catalytic processes. We have further demonstrated the LCR concept and utilized the unique pseudo-aromaticity of our PN<sup>3</sup>(P) platform to enhance the ligand reactivity. A pseudo-dearomatized PN<sup>3</sup>P\*Ni-H complex was synthesized as a new NHC-like ligand and  $\sigma$ -nucleophilic catalyst. Last but not least, a new class of 2<sup>nd</sup> generation of PN<sup>3</sup>P-pincer complexes was established (Figure 6). We anticipate that our discussion herein can provide better understanding of the PN<sup>3</sup>(P)-pincer ligand platform we established. Other unique reactivities of various transition metal complexes are expected to be discovered in the near future. The novel LCR that the imine arm reaches unprecedented carbene-like reactivity may open a new direction for the catalyst design. The properties and potentials of 2<sup>nd</sup> generation of PN<sup>3</sup>P complexes are awaiting further exploration.



**Figure 6.** Historical Development of the PN<sup>3</sup>(P)-pincer chemistry.



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## Notes

K.-W.H. declares the following competing financial interest(s): Huang is one of the inventors of US Patent# 8,598,351

"Phospho-amino pincer-type ligands and catalytic metal complexes thereof" assigned to KAUST.

# These authors contributed equally to this work.

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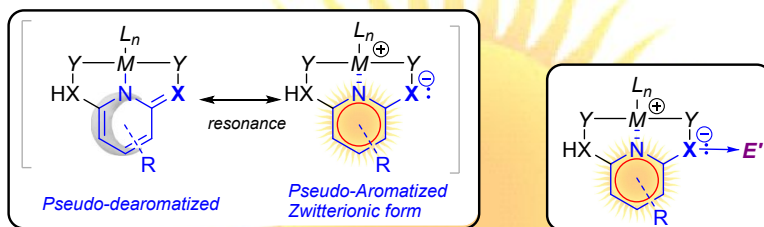
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SYNOPSIS TOC (Word Style "SN\_Synopsis\_TOC").



### Evolution of concepts

