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Review

A new class of PN^3 -pincer ligands for metal-ligand cooperative catalysis

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Abstract:

Work on a new class of PN^3 -pincer ligands for metal-ligand cooperative catalysis is reviewed. While the field of the pyridine-based PN^3 -transition metal pincer complexes is still relatively young, many important applications of these complexes have already emerged. In several cases, the PN^3 -pincer complexes for metal-ligand cooperative catalysis result in significantly improved or unprecedented activities. The synthesis and coordination chemistry of PN^3 -pincer ligands are briefly summarized first to cover the synthetic routes for their preparation, followed by a focus review on their applications in catalysis. A specific emphasis is placed on the later section about the role of PN^3 -pincer ligands' dearomatization-rearomatization steps during the catalytic cycles. The mechanistic insights from density functional theory (DFT) calculations are also discussed.

Keywords:

Metal-ligand cooperative catalysis, N-H bond, Dearomatization, Dehydrogenation, Hydrogenation, PN^3 -Pincer ligand

1. Introduction

A wide variety of transition metal complexes has been utilized as homogeneous catalysts in organic transformations involving chemical bond activation and formation events[1, 2]. One obvious advantage is that through modification of the ligand structures, it is possible to manipulate the ligation environment and tune the electronic properties of the metal centers to improve and achieve desirable stability, catalytic reactivity, chemo- and stereoselectivity. While in most cases, all the reactions occur only on the metal center in the form of oxidation additions, reductive eliminations, insertions, ligand substitutions, metathesis, etc. [1, 2], intriguing examples in which the ligand and the metal interact and work together in substrate activation have received increasing attention. These cooperating ligands are involved in a bond-breaking or/and forming step of the substrate or product through reversible chemical processes without the change in the oxidation state of the metal center. The metal center and the ligand interact with the substrate(s) in a synergistic manner and such interactions facilitate the chemical transformation that cannot be achieved with either the metal or the ligand alone.

Arguably, one of the most recognized examples of such a system is the metal-amine/amide system in the hydrogenation and transfer hydrogenation of C=O and C=N bonds [3-23]. The pioneering work by Noyori and co-workers demonstrated that a dramatic enhancement in the catalytic activity of the Ru complex in the hydrogenation of acetophenone was obtained when 1 equivalent of ethylenediamine and 20 equivalents of KOH were added into the reaction mixture, an increase of a turnover frequency (TOF) of less than 5 h⁻¹ to 6700 h⁻¹ [24]. Further optimization by varying the phosphine and amine ligands allowed excellent chemo- and stereoselectivities to be achieved. Experimental and computational mechanistic studies later confirmed that the active catalytic species contains a [Ru (phosphine)₂(ethylenediamine)] core structure. Upon treatment of a base in the presence of hydrogen, a ruthenium dihydride intermediate is formed. Hydrogenation of the ketone can proceed via a concerted ionic hydrogenation pathway by the Ru(H)-NH₂-R moiety. The resulting Ru-amide complex then facilitates the heterolytic cleavage of the hydrogen molecule or promote the deprotonation of a bonded η^2 -H₂ group to regenerate the ruthenium dihydride intermediate to complete a catalytic cycle [4] (Scheme 1). Related systems have been developed employing Rh, Ir, Fe, and Os. Significant progress has been made in extending the substrate scope to imides, amides, esters, epoxides, nitriles, activated olefins, and CO₂ [3-23].

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Scheme 1. Proposed metal-ligand cooperative mechanism for the Ru-amine catalyzed hydrogenation of ketones [23].

Remarkable reactivities in the activation of alkane C-H bonds were observed in early transition metal imido complexes ($(\text{R}'\text{O})_n\text{M}=\text{NR}$; $\text{M} = \text{Ti}, \text{Zr}, \text{Ta}, \text{and W}$). While experimental information is limited, theoretical investigations suggest a planar four-centered transition state where the cooperating imido group assists the cleavage of the unactivated C-H bond [25-30].

Scheme 2. C-H activation by the metal-ligand cooperation of the $\text{M}=\text{NR}$ complex [26].

In all of these reactions, metal-ligand cooperation events were observed only between the metal and the donor atom in the first coordination sphere. There are also extraordinary examples in which non-coordinating atoms in the ligand can participate in the substrate activation. Among them, the Shvo system is particularly interesting [31-35] (Scheme 3). The so-called Shvo catalyst is a bimetallic complex that contains a bridging hydride between two ruthenium atoms and a bridging proton between the two O substituted cyclopentadienyl (Cp) ligands. It catalyzes the hydrogenation (and transfer hydrogenation with formic acid) of the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds at elevated temperatures. Under these reaction conditions, this bimetallic complex is cleaved into a

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monometallic complex with a Ru-H bond and a hydroxyl group on the Cp ring. The hydrogenation can then occur by a concerted hydride transfer from the Ru center and a proton transfer from the OH substituent, i.e. ionic hydrogenation [36, 37]. Analogous Fe catalysts were studied by Casey and Guan with the Knölker complex which offered excellent tolerance to functional groups such as halides, nitro groups, benzyl ethers, and cyclopropyl rings [38, 39].

Scheme 3. Hydrogenation catalyzed by the Shvo catalyst [36].

One unique type of metal-ligand cooperation via aromatization-dearomatization of the central pyridine on pyridine-based pincer complexes via deprotonation-reprotonation of one of the pyridylic CH₂ arms was recently demonstrated by Milstein and co-workers [40-42]. Pincer-type metal complexes have been studied extensively in recent years as they offer several advantages to catalyst design [43-54]. The tridentate pincer ligands bind the metal center tightly typically in a meridional fashion, forming complexes with good stability. These ligands can be systematically modified to achieve desirable reaction activity and selectivity and thus serve as a perfect platform for catalyst development. These favorable properties are observed in Milstein's system in dehydrogenative reactions of alcohols utilizing the aromatization-dearomatization steps for substrate activation and catalyst regeneration. The Milstein's PNP-Ru complex (**MRu1**) was identified as an effective catalyst precursor in the presence of one equivalent of base for the dehydrogenation of secondary alcohols to ketones, with the formation of hydrogen as the sole byproduct. The same reaction condition is also applicable to the dehydrogenative coupling of primary alcohols to the corresponding esters in reasonable yields. A significant enhancement in the reactivity was achieved when one of the phosphine donors was replaced by a smaller and hemilabile amine group (**MRu2**) [55, 56]. When **MRu2** was treated with one equivalent of base, a dearomatized/deprotonated complex **MRu3** was produced. **MRu3** demonstrated the same catalytic activity but now in the absence of added base. This remarkable complex also catalyzes the dehydrogenative coupling of alcohols with amines to form amides and H₂. A plausible mechanism was proposed to involve the aromatization-dearomatization processes. **MRu3** activates the O-H bond of the alcohol to the aromatized hydridoruthenium alkoxide intermediate. The hemilabile amine arm then dissociates to leave a vacant coordination site to facilitate the β-

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hydride elimination to give the *trans*-dihydride complex (**MRu4**) which liberates H₂ to regenerate **MRu3** [57]. A recent computational study by Wang and co-workers revised the mechanism with a bifunctional double hydrogen transfer step but still supported the essential role of the ligand aromatization-dearomatization processes [58].

Scheme 4. Proposed mechanism for the dehydrogenative coupling reactions catalyzed by **MRu3** [42, 57].

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In sharp contrast to the incredible success met in the catalytic applications of PNN-Ru complexes, reports on other analogous pyridine-based pincer complexes are scarce. More specifically, even though the analogs of the PNP ligand, $P^N N^N P$, where the CH_2 spacers in PNP are replaced by NH ones, have been known for more than two decades since its first report by Haupt and co-workers, the investigation of the dearomatization process by deprotonating one of the NH groups has never been made and their potential catalytic applications were not evaluated until our recent work [59]. The fact that the N-H bonds are more acidic yet stronger than similar C-H bonds [60-62] makes it extremely interesting to interrogate what would occur if the CH_2 spacer(s) were replaced by NH group(s) (Table 1). We proposed to use PN^3 to denote this class of ligands because there are at least 3 “N” in all the known ligands and the “N” can be either a spacer or a coordinating atom: PN^3P for the symmetric ligands and PN^3X for the un-symmetric ones. Since there are currently only a limited number of published reports available at this stage, we will start by discussing the history of PN^3P ligands and their coordination chemistry followed by a thorough review of all catalytic applications involving the ligand aromatization-dearomatization steps. Mechanistic insights by density functional theory (DFT) calculations will also be highlighted and in the end conclusive remarks will be provided.

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

Table 1. Differences in BDEs between C-H and N-H bonds [62].

2. Synthesis and Coordination Chemistry of PN^3 -pincer ligands

2.1. Synthesis of PN^3 -pincer ligands.

2.1.1. Synthesis of symmetrical PN^3P ligands. Known PN^3P pincer ligands were listed in Scheme 5. These ligands could be prepared in a straightforward fashion starting from 2,6-diaminopyridine or 1,3,5-triazine-2,4-diamine with the respective chlorophosphine compound, R_2PCl , in the presence of a base, typically NEt_3 and/or n -BuLi [63-70]. The construction of P-N bonds was first reported by Haupt and co-workers and then was further expanded by the Kirchner group. A variety of substituents on the phosphines containing both bulky and electron-rich dialkyl could be obtained via deprotonation and nucleophilic substitution as described above. Notably, several P-O bond-containing achiral and chiral phosphine units could also be synthesized facilely (Scheme 5). A series of PN^3P -pincer ligands are thus easily available and accessible for the modification of steric, electronic, and chemical properties.

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Scheme 5. Typical symmetrical PN^3P -pincer ligands [68, 71].

2.1.2. Synthesis of unsymmetrical PN^3P -pincer ligands. The construction of unsymmetrical PN^3P -pincer ligands requires multiple-step synthesis, but the replacement of one of the phosphine groups by a different donor could allow further modification of the steric and electronic properties of the coordinated metal center, thus achieving desirable reactivity. Several kinds of unsymmetrical PN^3P -pincer ligands were designed and synthesized with this spirit in mind.

Scheme 6. Synthesis of **L18** [72].

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The first type of unsymmetrical pincer ligand containing a pendent amine donor was synthesized from 6-[(diethylamino)methyl]pyridin-2-amine by the treatment of NEt_3 and $n\text{-BuLi}$, followed by the addition of $t\text{Bu}_2\text{PCl}$. The desired crude product could be employed for metal complex synthesis without further purification [72] (Scheme 6).

Scheme 7. Synthesis of **L19** and **L20** [73].

The unsymmetrical PN^3 -pincer ligands with an oxazoline arm were also synthesized. Starting with the reaction of the commercially available 6-bromopicolinic acid and oxalyl chloride in tetrahydrofuran (THF), followed by the addition of amino alcohols in the presence of triethylamine afforded the amide products in high yields [73]. Amides were then treated with ammonium hydroxide in the presence of a copper catalyst to give the aminopyridine compounds. Replacement of the hydroxyl group by chlorine was achieved via the reaction with thionyl chloride and then the oxazoline rings were constructed through the deprotonation with sodium hydride for the intramolecular nucleophilic substitution. Phosphine functionality was installed with the typical method with $t\text{Bu}_2\text{PCl}$ in the presence of NEt_3 and $n\text{-BuLi}$ (Scheme 7).

Scheme 8. Synthesis of **L21** [74].

The unsymmetrical PN^3 -pincer ligand with a pyridine arm was also designed and synthesized. Upon the treatment of 6-bromo-2,2'-bipyridine under a high pressure of NH_3 in the

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presence of a Cu_2O catalyst, the amino product could be obtained. The phosphine group was introduced by the same procedure described above [74] (Scheme 8).

Scheme 9. Synthesis of **L22-L25** [75].

The route for the preparation of the unsymmetrical PN^3P -pincer ligands with a pyrazole arm was developed by using a symmetrical starting material with two different donors installed in two independent steps. 2-Bromo-6-(1H-pyrazol-1-yl)pyridine was synthesized by the reaction of 2,6-dibromopyridine and 1H-pyrazole in the presence of KOtBu . After the treatment of 2-bromo-6-(1H-pyrazol-1-yl)pyridine under a high pressure of NH_3 in the presence of Cu_2O in glycol, the amino intermediates were formed in good yields, to which a phosphine group was introduced later [75] (Scheme 9).

2.1.3. Synthesis of unsymmetrical PN^3P -pincer ligands. The Kirchner group introduced these two ligands recently. They could both be synthesized using a similar procedure to those for the symmetrical PN^3P -pincer ligands. Upon treatment of 2 equivalents of $i\text{Pr}_2\text{PCl}$ with the respective 2,6-diaminopyrimidine in the presence of NEt_3 in THF, these air-stable ligands were isolated in good yields (68-85%) [76] (Scheme 10).

Scheme 10. Synthesis of **L26** and **L27** [76].

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2.2 Coordination chemistry

2.2.1. First-row transition metals

2.2.1.1. Chromium. The first chromium(0) complex with a symmetrical PN^3P ligand (**L1**) was prepared by the Haupt group via mixing the ligand with 1 equivalent of $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ in tetrahydrofuran (THF) [63]. Based on the elemental analysis result, *mer*- $[\text{Cr}(\text{CO})_3(\text{L1})]\cdot 2\text{THF}$ (**Cr1**) was obtained. Attempts using $\text{Cr}(\text{CO})_6$ as the starting materials in the presence of trimethylamine oxide resulted in the oxidation of the **L1** ligand [64]. It was not until 2013 when the chromium (III) analog was synthesized by Gambarotta and co-workers by treating the same ligand with $\text{CrCl}_3(\text{THF})_3$ [77, 78]. The resulting complex *mer*- $\text{CrCl}_3(\text{L1})$ (**Cr2**) was characterized by single crystal X-ray crystallography. **Cr2** adopts an octahedral geometry and exhibit the expected magnetic moment of Cr(III) in this coordination environment. The same group also demonstrated that **Cr2**'s reactivity with alkyl aluminum is sensitively dependent on the nature of these reagents. **Cr2** was treated with 10 equivalents of diethyl aluminum chloride (DEAC) to give a cationic trivalent chromium complex (**Cr3**) with the Cr monoalkylated and the N-H arms intact. When 5-10 equivalents of trialkyl aluminum reagents were employed, deprotonation of one of the amine groups was observed. The reaction of **Cr2** and trimethyl aluminum yielded a monomethyl Cr(III) complex with one of the amine arms deprotonated and coordinated to a ClAlMe_2 group. In the cases of more reducing triethyl- and tri-*i*-butylaluminum, divalent Cr complexes (**Cr4** and **Cr5**) also with one deprotonated amine function coordinated to a ClAlR_2 group were obtained presumably due to the decreased stability of the initially formed monoalkyl chromium(III) species (Scheme 11). A similar Cr(II) complex was prepared by reacting $\text{Cr}(\text{II})\text{Cl}_2$ with 5 equivalents of DEAC, and the amine arms were not deprotonated. The synthetic procedure for *mer*- $\text{CrCl}_3(\text{L1})$ is applicable to other unsymmetrical PN^3 -ligands. A series of Cr(III) complexes was also prepared accordingly [75] (Figure 1).

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Scheme 11. Synthesis of **Cr2** and the reactivity toward alkyl aluminum reagents [63, 77, 78].

Figure 1. A series of new $\text{PN}^3\text{-Cr(III)}$ complexes [75].

2.2.1.2. Iron. PN^3P -iron complexes have been extensively and elegantly studied by the Kirchner group [68]. The initial synthesis started with the hexaquo complex $[\text{Fe}(\text{H}_2\text{O})_6](\text{BF}_4)_2$. Upon complexation with the PN^3P ligands in CH_3CN , a series of octahedral diamagnetic $[\text{PN}^3\text{P-Fe(II)(MeCN)}_3]^{2+}$ complexes were obtained (**Fe1-Fe6**). The presence of water did not cause any decomposition of the ligands or Fe(II) products. The nitrile ligands in these complexes can be substituted by bidentate and tridentate nitrogen ligands, and CO. **Fe1** reacts with bipyridine (bpy), terpyridine (terpy), or another molecule of PN^3P to afford complexes **Fe7-Fe9** (Scheme 12). Interestingly, upon reaction with CO, **Fe1** and **Fe2** form only the mono-substituted products, monocarbonyl complexes **Fe10** and **Fe11**, respectively, without formation of any dicarbonyl

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Fe(II) complexes. When **Fe3-Fe6** were subjected to the same condition, no CO coordinated product was formed, indicating that the stronger π -accepting phosphines decreased the Fe center reactivity toward CO substitution.

Scheme 12. Synthesis and reactivity of PN^3P -Fe complexes [68].

Coordinationally unsaturated paramagnetic ($S=2$) Fe(II) complexes (**Fe12** and **Fe13**) were achieved by the reaction of $\text{PN}^3\text{P}^{t\text{Bu}}$ (**L4**) and $\text{PN}^3\text{P}^{i\text{Pr}}$ (**L5**) ligands with FeCl_2 , respectively [76, 79, 80] (Scheme 13). The pentacoordinate geometry of **Fe13**·THF was confirmed by the X-ray single crystal structure which also suggests that “basal” (considering a distorted square pyramid) chloride leads to a hydrogen-bond interaction with one of the N-H moieties of the neighboring complex. A distorted diamond-type three-dimensional network with incorporated THF molecules was formed by these intermolecular H-bonds. The light yellow **Fe13** reacted rapidly with CO to

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afford the deep red diamagnetic complex, *cis*-Fe(**L5**)(CO)(Cl)₂ (**Fe14**) as the only product. Similar observations were made for analogous Fe(II) complexes with ligands **L26** and **L27**. The formation of **Fe14** was much slower when the **Fe13**·THF single crystals were used. Strikingly, the blue diamagnetic complex, *trans*-Fe(**L5**)(CO)(Cl)₂ (**Fe15**) was formed when the **Fe13** reacted with CO in an acetone solution. Both **Fe14** and **Fe15** lost CO upon heating at 100 °C *in vacuo* to generate analytically pure **Fe13**, indicating that the CO association and dissociation process is fully reversible. In DMSO, **Fe14** can be converted to **Fe15** within 90 mins, and the chloride dissociation was proposed to initiate this isomerization. In a recent study, a dicarbonyl Fe(II) complex, *trans*-[Fe(**L5**)(CO)₂Cl]⁺ (**Fe16**) was prepared and its reaction with Zn resulted in the formation of a Fe(II) monohydride *cis*-[Fe(**L5**)(CO)₂H]⁺ (**Fe17**) [81] (Scheme 14). Mechanistic investigations suggest that this transformation involves the heterolytic cleavage of the hydrogen molecule produced during the reaction via Fe-Ligand cooperation (see section 4).

Scheme 13. Synthesis and reactivity of **Fe12** and **Fe13** [76, 79, 80].

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Scheme 14. Heterolytic cleavage of H₂ [81].

2.2.1.3. Nickel. Square-planar PN³P Ni(II) complexes were obtained by reacting nickel(II) halide salts/complexes with the PN³P ligands. Haupt and co-workers prepared [Ni(**L1**)Cl]Cl (**Ni1**) by adding the **L1** ligand to NiCl₂·6H₂O in ethanol [63]. Analogous bromide complexes were synthesized by the Kirchner group from the PN³P ligands and NiBr₂(DME) (**Ni2-Ni4**, R = Ph, *i*Pr, and *t*Bu) [68] (Scheme 15). These complexes remained stable thermally and in air for several months. However, adapting the same protocol for phosphoramidite-type PN³P ligands resulted in a different story. The formation of square pyramidal nickel(II) complexes containing an *in situ* formed anionic phosphinito ligand, R₂P(O)[−], was observed. Based on experimental findings at a Ni to the PN³P ligand ratio of 1:1.5, it was proposed that the R₂P(O)[−] ligand was regenerated from the hydrolysis of the aminophosphine bond when the PN³P ligand was bonded to Ni. The coordination to Ni enhanced the electrophilicity of the phosphine groups, allowing them to be attacked by water [82] (Scheme 16).

Scheme 15. Synthesis of PN³P-Ni complexes [68].

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Scheme 16. Proposed mechanism of the hydrolysis reaction [82].

2.2.1.4. Copper. CuI reacts with one equivalent of the **L1** ligand in THF to generate a dimeric Cu(I) complex (**Cu1**) in 77% yield. Its molecular structure was elucidated by single-crystal X-ray crystallography [83]. Each copper atom is tetracoordinated by the pyridine nitrogen and one of the phosphine donors from one PN³P ligand, one of the phosphine donors from the other PN³P ligand, and one iodide. Interestingly, the corresponding ³¹P NMR spectrum only shows one sharp singlet signal at δ 27.3 ppm, suggesting that all the phosphine groups are equivalent in the *d*₆-DMSO solution. When 2 equivalents of **L1** was used to react with CuI, a new cationic complex (**Cu2**) was obtained (Scheme 17). While the quality of the crystallographic data was not good enough for structural refinement, the preliminary solution showed a tetracoordinated Cu center with two **L1**, each of which served as a bidentate ligand with the pyridine nitrogen and one of the phosphine donors bound to the Cu(I) center. The corresponding ³¹P NMR spectrum shows no signal for the free phosphine groups, but two singlet peaks at δ 16.3 and 17.2 ppm, indicative of a fast coordinating equilibrium between all phosphine arms in the solution.

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Scheme 17. Synthesis of PN^3P -Cu complexes [83].

2.2.2. Second Row transition metals

2.2.1.1 Molybdenum. The pioneering work of the PN^3P pincer molybdenum complexes were performed by Haupt and co-workers [63]. *mer*- $[\text{Mo}(\text{CO})_3(\text{L1})] \cdot 2\text{THF}$ (**Mo1**) was formed via the reaction of *fac*- $\text{Mo}(\text{CO})_3 \cdot (\text{CH}_3\text{CN})_3$ and the **L1** ligand. This complex was characterized by ^{31}P and ^1H NMR. The molecular structure of this complex was determined as an octahedral complex containing a nearly planar tridentate chelating pincer ligand. Other analogous molybdenum complexes were also synthesized. These complexes could undergo oxidative addition with halogens. For instance, the reactions with Br_2 or I_2 and the PN^3P -Mo complexes in CH_2Cl_2 were able to give the products **Mo5** and **Mo6**. Interestingly, the mono(acetonitrile) complex **Mo7** was obtained when the reaction was performed in acetonitrile [68, 84] (Scheme 18). Notably, these results represent the first seven-coordinate molybdenum pincer complexes reported. In addition to the spectroscopic characterization, the solid state structures of molybdenum complexes (**Mo1** and **Mo3**) were determined by X-ray diffraction. The coordination geometry around the molybdenum center corresponds to a distorted octahedron.

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Scheme 18. Synthesis of PN³P-Mo complexes [63, 68, 84].

2.2.1.2. Ruthenium. The preparation of various symmetrical ruthenium PN³P complexes was achieved by reacting RuCl₂(PPh₃)₃ with the respective ligands [68] (Scheme 19). However, no reaction occurred when **L4** was used as the ligand, presumably due to the bulkiness of the *t*Bu groups. As a result of the rigidity of PN³P pincer ligands, only the *mer*-PN³P-Ru complex with either a *trans*- or *cis*-dichloro arrangement was obtained. A mixture of both structures was not observed.

Scheme 19. Synthesis of PN³P-RuCl₂(PPh₃) complexes [68].

Treatment of the PN³P ligand with RuHCl(PPh₃)₃(CO) in THF at 65°C for 12 h yielded **Ru7** as a pale yellow solid [59] (Scheme 20). The ¹H NMR spectrum showed one triplet at δ - 26.11 ppm indicating the existence of a hydride. The reaction of complex **Ru7** with one equivalent of *t*BuOK afforded a dearomatized complex (**Ru12**). The ¹H NMR spectrum showed

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the appearance of a new N-H group at δ 4.23 ppm as well as a set of sp^2 C-H signals at δ 5.17, 6.76, and 6.89 ppm, indicating the dearomatization of the pyridine ring. The ^{31}P NMR spectrum also supported the dearomatized structure with two doublets at δ 127.4 and 130.5 ppm. Most importantly, this was the first time that a unique dearomatization process of the central pyridine ring was demonstrated. Employing the same strategy, other PN^3 -pincer complexes were synthesized successfully [72-74].

Scheme 20. Synthesis of PN^3 -Ru(H)(CO)Cl complexes [59, 72-74].

2.2.1.3 Palladium. Treatment of Pd(cod)Cl_2 with the various symmetric PN^3P ligands in CH_2Cl_2 for 2 h afforded cationic, tetracoordinated, square-planar palladium complexes [63, 68] (Scheme 21). In those complexes with poor solubility toward most organic solvents, a counterion exchange was carried out with the halide scavenger KCF_3SO_3 in CH_3CN to achieve good solubility.

Scheme 21. Synthesis of PN^3P -Pd complexes [63, 68].

These PN^3P -Pd complexes are stable in air both in the solid state and in solution. Nonetheless, the P-N bond can be cleaved when it is exposed to air in the DMF solution at room temperature for several days. The product was determined to be a neutral, square-planar complex, containing an anionic phosphinito ligand and a bidentate PN ligand derived from the decomposition of the previous ligand [82] (Scheme 22).

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Scheme 22. Hydrolysis of complex **Pd4** [82].

2.2.3. Third-Row transition metals

2.2.3.1. Tungsten. The first W(0) complex, W(**L1**)(CO)₃ (**W1**) was synthesized by Haupt and co-workers by reacting 1 equivalent of W(CO)₃(CH₃CN)₃ with ligand **L1** in 22% yield [63]. An alternative method was developed by the Kirchner group to obtain a tungsten(II) complex [W(PN³P)(CO)₃Br]Br in 60-80% yield via the known complex W(CO)₄(μ-Br)Br₂ [84]. Several PN³P ligands were used to obtain the corresponding W(II) complexes (**W2-W4**). A reducing reagent was required to convert W(II) complexes into W(0) complexes. Since the use of Zn resulted in the formation of highly soluble salts difficult to be removed, complex **W2-W4** were treated with an excess of 10% NaHg in THF to give the W(PN³P)(CO)₃ complexes (**W5-W7**) in 70-80% isolated yields, significantly improved from Haupt's procedure. When adding HBF₄ into the CH₂Cl₂ solution of complexes **W5-W7**, protonation at the tungsten center occurred to afford hydrido W(II) complexes (**W9-W10**) (Scheme 23). The protonation process was reversible upon addition of NEt₃. The seven-coordinate complex **W8**·BF₄ was characterized by the single crystal X-ray crystallography (Figure 2). Its coordination geometry showed a distorted hydride-capped octahedron around the W center. The hydride ligand pushes the carbonyl group positioned in the metal-ligand plane toward the adjacent phosphine group. The less symmetrical geometry results in the fluxional behavior of the W(II) hydride complex in solution.

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Scheme 23. Synthesis and reactivity of $\text{PN}^3\text{P-W}$ complexes [84].

Figure 2. Solid state structure of **W8** [84].

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2.2.1.2. Iridium. Iridium complexes were prepared by the Kempe group by adding an $[\text{IrOMe}(\text{cod})]_2$ solution to the pre-generated PN^3P ligand in THF [71] (Scheme 24). Using different types of ligands, a series of PN^3P -Ir(cod) complexes were obtained (**Ir1**-**Ir3** for **L5**, **L15**, and **L16**, respectively). Complex **Ir3** was characterized by single-crystal X-ray crystallography (Figure 3) [71]. Interestingly, no evidence for dearomatization was observed in the solid state structure containing an anionic N-PR_2 arm (Note: DFT results suggest the dearomatization, see section 4). However, when an excess amount of primary alcohols was added, Ir(III) trihydride (**Ir4**) was formed via the alcohol dehydrogenation. The Huang group also used 0.5 equivalent of $[\text{Ir}(\text{coe})_2\text{Cl}]_2$ as the metal source to react with **L4** in toluene at room temperature to afford complex **Ir5** in 90% yield. Treatment of **Ir5** with 1.5 equivalents of $\text{KO}t\text{Bu}$ led to the formation of **Ir6**, again containing an anionic PN^3P ligand in the solid state structure [85] (Scheme 24). In solution, however, the ^1H NMR analysis suggested that the pyridine ring in **Ir6** underwent dearomatization. Remarkably, these Ir complexes were sensitive toward oxygen and water for weeks; they could thus be handled in air.

Scheme 24. Synthesis and reactivity of PN^3P -Ir complexes [71, 85].

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Figure 3. Structural view of complex **Ir3**•THF showing 50% thermal ellipsoids (H atoms omitted for clarity). Selected bond lengths (Å): N1–C(9) = 1.37(2), N1–C(10) = 1.36(2), N2–C(10) = 1.34(2), N2–C(17) = 1.32(2), N3–C(17) = 1.45(2), N3–C(9) = 1.41(2) [71].

2.2.3.3. Platinum. Analogous PN³P-Pt complexes were prepared from [Pt(cod)Br₂] in the similar manner as the Pd complexes (Scheme 25). Their reactivities have not yet been widely explored, but they show good thermal and air stability both in the solid state and in solution [68].

Scheme 25. Synthesis of PN³P-Pt complexes [68].

2.2.3.4. Gold. The reaction of 2 equivalents of Au(SMe₂)Cl and 1 equivalent of **L1** gave the corresponding bimetallic [(**L1**)Au₂Cl₂] complex (**Au1**), according to a similar strategy used to generate other gold(I) phosphine complexes [83, 86]. **Au1** was then treated with an Ag⁺ agent to remove the chloride to prepare the cationic Au species in the presence of 2nd equivalent of **L1** to

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afford a bimetallic macrocyclic complex **Au2**. The molecular structure of **Au1** was determined by the single crystal X-ray diffraction, but that of **Au2** was postulated based on spectroscopic analysis.

Scheme 26. Synthesis of PN^3P -Au complexes [83, 86].

3. Applications in Catalysis

3.1. Transfer hydrogenation under base-free conditions.

3.1.1. *Transfer hydrogenation catalyzed by a dearomatized PN^3P ruthenium pincer complex.* Ruthenium catalyzed transfer hydrogenation reactions of ketones with 2-propanol (*i*-PrOH) have been well studied [3, 5, 87-92]. The advantages of these reactions include their notable convenience for larger-scale synthesis, and reaction conditions free of high hydrogen pressure and hazardous reducing agents. Inspired by these outstanding results, the new PN^3P -pincer ruthenium complexes were examined for transfer hydrogenation [59] (Table 2).

Table 2. Selected data for the transfer hydrogenation of ketones by ruthenium complexes.^a [59]

$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3 \xrightarrow{\text{Cat.}} \text{R}^1-\text{CH}(\text{OH})-\text{R}^2 + \text{CH}_3\text{C}(=\text{O})\text{CH}_3$				
Entry	Substrate	Product	Time/h	Yield(%) ^b
1 ^c			16	-
2			16	100(91)
3			16	93(89)
4			16	69 alcohol 14 styrene
5			16	82 alcohol 12 <i>p</i> -bromo-styrene

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^a Conditions: Complex **Ru12** (0.01mmol), ketone (1.0 mmol), and 2-propanol (2.0 ml), T = 82 °C under argon. ^b Determined by GC, isolated yield in parentheses. ^c Complex **Ru7** (0.01mmol).

Aromatic complex **Ru7** was not effective for the reaction (Table 2, entry 1), while complete conversion to cyclohexanol was afforded within 16 h by using dearomatized complex **Ru12** as the catalyst (Table 2, entry 2). Complex **Ru12** also exhibited higher reactivity to aliphatic ketones (Table 2, entry 3). Aromatic ketones could also be hydrogenated albeit with the formation of a small amount of styrene as the side products (Table 2, entry 4 and 5).

The dearomatized complex was necessary for the reaction as demonstrated by the results from entries 1 and 2. A plausible mechanism was proposed according to previous reports (Scheme 27). Initially, hydrido ruthenium alkoxide species **I** may be formed by the reaction of complex **Ru12** and *i*-PrOH via proton transfer from O to N. Subsequently, the dihydride species **Ru17** may be generated via β -hydride elimination to expel one acetone molecule. The reaction of the ketone substrate and **Ru17** could then occur by the insertion into the Ru-H bond of **Ru17** to afford a new hydrido ruthenium alkoxide species **II**. Deprotonation of one of the NH arms by the alkoxide moiety of **II** forms the alcohol and regenerates the active catalyst **Ru12**. The oxidation state of the ruthenium complexes did not change during the overall process. This protocol is the first case of reversible dearomatization/rearomatization via deprotonation/reprotonation of the NH spacer on the PN^3P ligand with no change in the formal oxidation state of the metal center. Complex **Ru12** showed good catalytic reactivity for the transfer hydrogenation of ketones.

Scheme 27. Proposed mechanism for transfer hydrogenation of ketones catalyzed by **Ru12** [59].

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3.1.2. Transfer hydrogenation catalyzed by a dearomatized PN^3 -pincer ruthenium complex with an oxazoline arm. In the proposed mechanism for **Ru12** catalyzed hydrogenation, in order to allow the β -hydride elimination to give the dihydride intermediate or the coordination of the ketone substrate for the Ru-H insertion, one of the phosphine arms has to dissociate. Based on this idea, a weaker donor may facilitate this process and thus boost the catalytic activities. Oxazolines are generally considered as weak donors and pincer complexes with one or two oxazoline groups have been widely used and received much attention considering their easy accessibility from amino alcohols. The strategy that combines an aminophosphine donor and an oxazoline ring in the PN^3 -pincer ligand design resulted in a ruthenium complex with significantly enhanced activities in the transfer hydrogenation of ketones compared to that of **Ru12**. The reactivities of the new complexes **Ru9** and **Ru10** toward the transfer hydrogenation were studied [73] (Table 3). Aromatic ruthenium complexes **Ru9** and **Ru10** showed excellent reactivities at 40 °C only in the presence of a base, indicating that the deprotonation of the ruthenium complexes was crucial during the catalytic cycle (Table 3, entries 1-4). The deprotonated ruthenium complex **Ru15** was synthesized and it exhibited excellent catalytic activity under base-free conditions at 40 °C (Table 3, entry 5), which was lower in temperature and shorter in reaction time compared with the results from a symmetrical ruthenium complex with the **L1** ligand. The dearomatized **Ru15** could be applied to a variety of substrates. The desired products were obtained in excellent yields for cycloketones and 2-alkylketones (Table 3, entries 5 and 6). Aromatic ketones can be hydrogenated to the corresponding alcohols in moderate to good yields (Table 3, entries 7). This simple modification of the ligand showed a clear difference in the catalytic reactivity of the dearomatized PN^3 -Ru complexes. Well-defined ruthenium complexes bearing both a strong and bulky phosphine and a weak and small oxazoline donor exhibited significantly improved catalytic activity for transfer hydrogenation.

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Table 3. Selected data for the transfer hydrogenation of ketones with Ru complexes.^a[73]
$$\begin{array}{c}
 \text{R}^1-\text{C}(=\text{O})-\text{R}^2 + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow[\text{iPrOH}]{\text{Catalyst}} \text{R}^1-\text{CH}(\text{OH})-\text{R}^2 + \text{CH}_3\text{CH}_2\text{CHO}
 \end{array}$$

Entry	Catalyst	Substrate	Time	Yield (%) ^b
1	Ru9	cyclohexanone	16 h	0
2 ^c	Ru9	cyclohexanone	16 h	96
3	Ru10	cyclohexanone	16 h	0
4 ^c	Ru10	cyclohexanone	16 h	98
5	Ru15	cyclohexanone	16 h	99
6	Ru15	2-hexanone	16 h	94
7	Ru15	4'- <i>tert</i> -butylacetophenone	16 h	61

^a Reaction conditions: 0.5 mmol of ketone, 1.0 mol% of Ru complex in 1.0 mL of *i*PrOH at 40 °C; ^b Determined by GC-MS or ¹H NMR spectroscopy, isolated yield in parentheses; ^c 1.0 mol% of KO^tBu was added.

3.2. Dehydrogenative homo-coupling of primary alcohols to esters. Dearomatized PN³-pincer ruthenium complexes catalyzed dehydrogenative homo-coupling of primary alcohols to esters was also investigated. Esterification is one of the most central and significant reactions in organic synthesis. Several environmentally friendly methods have been developed where the use of condensing reagents and activators and the formation of waste byproducts can be avoided. Dehydrogenative coupling of alcohols to esters with the release of H₂ is an appealing goal. Milstein's Ru catalyst (**MRu2**) has shown superior activity in this reaction. With the structural similarity, the catalytic activities of dearomatized PN³-Ru complexes were tested. **Ru12**, **Ru13** and **Ru15**, exhibited good to excellent reactivities for the dehydrogenative homo-coupling of primary alcohols (Table 4). Several linear aliphatic alcohols and benzyl alcohol could be converted into the corresponding esters effectively with catalyst **Ru15** [72].

Table 4. Selected data for the esterification of primary alcohol with ruthenium complexes.^a[72]

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Entry	Catalyst	Alcohol	cat. (mol%)	T (°C)	Time	Conv. ^b
1	Ru12		0.1	160	24 h	80%
2	Ru13		0.1	160	24 h	60%
3	Ru15		0.1	160	24 h	98%

^a Under argon. ^b Determined by GC and ¹H NMR.

After the dehydrogenative coupling of primary alcohols to esters was achieved in high yields at 110-160 °C, the extension of this system to alcohols with lower boiling points was also investigated, such as ethanol and 1-propanol. Among them, the product from ethanol dehydrogenation, ethyl acetate (EA), is an important petrochemical, widely used as a solvent or reaction intermediate in industry. Direct formation of EA from ethanol could potentially relieve our demand for petrochemicals since ethanol can be obtained from biomass. However, challenges exit, especially with the aim of higher conversion to avoid the need for the separation of the ester products from the reaction mixtures, due to the required high reaction temperature and the equilibrium limit in a closed system. A defect-free Pd-Ag membrane reaction was thus designed for the removal of the liberated hydrogen *in situ*, enabling the reaction to proceed at elevated temperatures and to reach quantitative conversion and EA production yields [93]. Furthermore, both of the liberated H₂ fluxes and the inner pressure of the reactor could be used to monitor the reaction progress in real-time. This could be applied to kinetic studies of other dehydrogenative reactions.

3.3. Coupling of amines to imines under oxidant-free conditions. Encouraged by the progress in the dehydrogenative ester formation, the catalytic activities of dearomatized PN³-Ru complexes were examined toward the dehydrogenative coupling of alcohols and amines to amides, for which the Milstein catalyst **MRu2** has shown superior activity. Very interestingly, even though a recent demonstration by the Hong group has suggested that by simply mixing 5 mol% of RuCl₃ precatalyst with carbene ligands [94], such a transformation could also be achieved. Indeed, dearomatized PN³-Ru complexes with similar geometries to that of **MRu2** gave very poor reactivities. The amide products were only generated in low yields, along with the observation of a mixture of imines and esters (Scheme 28). It was concluded that the dearomatized PN³-Ru complexes possess an enhanced reactivity toward amine dehydrogenation. The surprising finding

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led to the discovery that the dearomatized symmetric complex **Ru12** showed the highest reactivity for selective imine formation (Table 5). Milstein's catalyst **MRu2** showed a much lower reactivity for the same reaction. Various benzyl amine substrates were explored with the formation of imines in good to excellent yields. Moreover, the cross-coupling of benzyl amines and anilines could also be achieved [72] (Table 5).

Scheme 28. Product analysis at low conversion [72].

Table 5. Selected data for dehydrogenative imine formation catalyzed by ruthenium complexes.^a[72]

$\text{R-CH}_2\text{NH}_2 \xrightarrow{\text{Ru complex}} \text{R-CH=N-CH}_2\text{R} \quad (+ \text{H}_2 + \text{NH}_3)$				
Entry	Catalyst	Amine	Product	Yield ^b
1	Ru12			93% (90%)
2	Ru13			71%
3	Ru15			90%
4	M2			49%

^a Conditions: Ruthenium complex (1.0 mol%), amine (1.0 mmol), in 2.0 mL of toluene at 110 °C under argon. ^b ¹H NMR yields (isolated yields in parentheses).

Based on these experimental results, a mechanism was proposed (Scheme 29). The dearomatized Ru complex dehydrogenates the primary amine to form the intermediate **IV** and the benzaldimine. The benzaldimine then reacts with another equivalent of amine to form the

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imine product with the elimination of one ammonia molecule. Catalyst **Ru12** is generated after the release of hydrogen from **IV**.

Scheme 29. A plausible mechanism for the dehydrogenative coupling reaction of amines to imines [72].

3.4. PN^3 -Ru complexes catalyzed hydrogenation of esters. Reduction of esters to the corresponding alcohols serves as one of the most important processes in organic synthesis. These reactions are usually performed with the use of stoichiometric or excess amounts of metal hydride reducing reagents, along with the formation of metal salt wastes. The direct hydrogenation of esters represents a more environmentally friendly approach. Milstein and co-workers have shown that **MRu2** catalyzed the hydrogenation of non-activated esters to corresponding alcohols under relatively mild and neutral conditions. The PN^3 -Ru complexes were examined for the hydrogenation of esters [74] (Table 6). The symmetrical PN^3 ruthenium complex **Ru7** showed poor reactivities, but the unsymmetrical PN^3 -Ru complexes, **Ru8-Ru11** exhibited good reactivities with the formation of the desired alcohols in comparable yields (Table 6, entries 2-5). Almost quantitative yields of benzyl alcohol and ethanol were afforded after the increase of the hydrogen pressure to 120 psi or higher. Since PN^3 -Ru complexes are in general not reactive toward water, the ethyl benzoate could also be fully hydrogenated to benzyl alcohol and ethanol even when 100 mg of water was added into the reaction mixture, suggesting that solvents without strict purification could be used for the hydrogenation under these conditions. Remarkably, the reaction time could be shortened to two hours using 400 psi of hydrogen. The hydrogenation of non-activated esters could be catalyzed by **Ru11** under optimized reaction conditions (Table 7). Interestingly, the hydrogenation of a bulky ester could

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proceed smoothly, even though it has been demonstrated as a poor substrate when using Milstein's catalyst.

Table 6. Hydrogenation of esters catalyzed by ruthenium complexes.^a[74]

entry	catalyst	conv (%) ^b	products (yiled [%]) ^b
1	Ru7	< 5	-
2	Ru8	73	benzyl alcohol (70), ethanol (69)
3	Ru9	65	benzyl alcohol (62), ethanol (63)
4	Ru10	71	benzyl alcohol (68), ethanol (68)
5	Ru11	75	benzyl alcohol (73), ethanol (70)
6	Ru11^c	>99	benzyl alcohol (98), ethanol (97)
7	Ru11^d	>99	benzyl alcohol (98), ethanol (97)
8	Ru11^e	>99	benzyl alcohol (98), ethanol (98)

^a Conditions: Ru catalyst (10 μ mol), KO^tBu (80 μ mol), and ethyl benzoate (1.0 mmol) in toluene (4.0 mL) was heated at 120°C under 81 psi of H₂ for 12 hr. ^b Conversions and yields were determined by GC and ¹H NMR. ^c H₂ pressure was increased to 120 psi. ^d 100 mg of water was added into the reaction mixture under 120 psi of H₂. ^e H₂ pressure was increased to 400 psi and the reaction time was shortened to 2 hr.

Table 7. Selected data for the hydrogenation reaction of unactivated esters.^a[74]

entry	ester	conv. (%) ^b	products (yiled [%]) ^b
1		99	(98), (98)
2		99	(98)
3		99	(96)

^a Conditions: Ruthenium complex **Ru11** (10 μ mol), KO^tBu (80 μ mol), and ester (1.0 mmol) in toluene (4.0 mL) was heated at 120°C under 400 psi of hydrogen for 2 hours. ^b Conversion of esters and yield of alcohols were determined by GC and ¹H NMR.

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3.5. PN^3 -Cr(III) complexes catalyzed ethylene oligomerization and polymerization. Polyethylene is a significant and ubiquitous material that plays an important role in our lives. The huge market demand for high performance polyethylene has driven extensive research efforts in industry and academia. Heterogeneous chromium catalysts have played central roles in polyethylene production, and homogeneous chromium catalysts have been widely developed. As a result, homogeneous molecular chromium catalysts for ethylene polymerization have drawn much research attention. PN^3 -Cr(III) complex **Cr2** catalyzed oligomerization of ethylene was studied by Gambarotta and co-workers. The presence of the pyridine substituent may stabilize the lower oxidation states of Cr. To further understand the catalytically active species, complex **Cr2** was treated with stoichiometric amounts of alkylaluminum activators. The trivalent oxidation state of chromium was preserved. The deprotonation of one of the two amino functions and the methylation of the chromium center occurred [77, 78].

The reactivities of the PN^3 -pincer chromium complexes in ethylene polymerization were also investigated for **Cr6**-**Cr10**. Only polyethylene was obtained with moderate activities without any detectable oligomers when the polymerization was carried in the presence of MAO or trialkylaluminum. The highest activity was achieved with the symmetrical **Cr6** complex at room temperature. Linear solid polyethylenes with molecular weights (M_w) from 12,300 to 63,200 were afforded without the formation of oligomers, clearly in sharp contrast to most of the PNP and NNN systems. Upon treatment with MAO, the formation of CH_4 was detected. Thus, the N-H group may be deprotonated and then a dearomatized intermediate is formed [75]. However, whether the dearomatized imine arm plays a role cannot be assessed at this time (Scheme 30).

Scheme 30. The proposed mechanism for the ethylene polymerization catalyzed by **Cr6** [75].

3.6. PN^3 -Ir pincer complex catalyzed selective α -alkylation of unactivated amides with primary alcohols. An efficient and robust iridium pincer complex for the selective α -alkylation of tertiary and secondary acetamides formed from a “borrowing hydrogen” methodology has been developed using **Ir5** and **Ir6** [85] (Scheme 31). The α -alkylation of amides is of significance and has been widely applied in the synthesis of biologically active products. On the other hand, alcohols are good alkylating reagents due to their less expensive and more environmentally friendly nature from the viewpoint of the chemical and pharmaceutical industries. Moreover, the

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only byproduct for such an alkylation processes is just water. The reactions of alcohols and unactivated acetamides with a variety of functional groups could be catalyzed by the aromatic iridium complex **Ir5** in the presence of a base, potassium *t*-butoxide (KO^tBu). The efficiency of this transformation sensitively depended on the amounts of KO^tBu. No desired products were observed in reactions with relatively weaker bases, such as Cs₂CO₃ and K₂CO₃. The concentration of the reaction has a minimal effect on the efficiency. This process is the first reported catalytic α -alkylation of unactivated acetamides with primary alcohols.

Scheme 31. The PN³ type of iridium pincer complex catalyzed selective α -alkylation of unactivated amides with primary alcohols [85].

As discussed above, to determine the active catalytic species, the aromatic complex **Ir5** was treated with KO^tBu at 120°C to afford a new iridium complex, **Ir6**, and the pyridine ring in complex **Ir6** believed to undergo dearomatization according to the ¹H NMR analysis in solution. The catalytic reactivity of complex **Ir5** was lower and complex **Ir6** showed good reactivity toward the oxidation of benzyl alcohol (Scheme 32). These observations suggested that the dearomatic PN³P-Ir complex is a plausible active catalytic species.

Scheme 32. The catalytic reactivities of **Ir5** and **Ir6** toward alcohol dehydrogenation [85].

3.7. PN³P-Ir complexes catalyzed sustainable acceptorless dehydrogenative couplings. Pyrroles are a class of useful compounds and could be found in many biologically active products, drugs, catalysts and materials. Many catalytic protocols have been developed for the synthesis of pyrroles. However, pyrrole synthesis that uses renewable resources is still highly desirable due to the high demand for these compounds. PN³P-Ir complex (**Ir3**) catalyzed pyrroles synthesis was achieved in which secondary alcohols and amino alcohols were deoxygenated and linked via selective successive formations of C-C and C-N bonds. The catalytic process can tolerate various functional groups and can proceed under mild reaction conditions [71] (Scheme 33). It was

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proposed that the secondary alcohol was oxidized (dehydrogenated) to form a ketone intermediate. Subsequently, the condensation of the ketone and the amino alcohol may afford the imine compound. The cyclization then occurs via the loss of hydrogen and water followed by the isomerization to the pyrrole structure (Scheme 34).

Scheme 33. Synthesis of 2,5-disubstituted pyrroles from secondary alcohols and amino alcohols [71].

Scheme 34. The process of catalytic pyrrole synthesis [71].

A mechanistic investigation showed that the catalyst resting state might be an aromatic iridium trihydride complex which might be formed by reacting catalyst **Ir3** with alcohols or H_2 . Furthermore, the base was identified to play an important role in catalytic pyrrole synthesis. Without the addition of a base, no desired product was afforded under the otherwise same conditions. More detailed discussion will be provided in Section 4. Acceptorless dehydrogenative alkylations have also been developed for the synthesis of benzimidazoles and quinoxalines with [95] (Scheme 35). Water and two equivalents of hydrogen are liberated during the course of the reactions.

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Scheme 35. Synthesis of benzimidazoles and quinoxalines from aromatic diamines and alcohols [95].

4. Mechanistic insights into the catalysis

Although the catalytic activities of pincer complexes containing $-\text{CH}_2\text{PR}_2$ substituents have been widely investigated during the last decade and potential applications have been highlighted in several cases, the mechanistic understanding behind their different activities have not been explored at the molecular level until recently. The replacement of $-\text{CH}_2\text{PR}_2$ groups by $-\text{NHPR}_2$ groups is not simply a geometric variant. Theoretical calculations should elucidate the influences of thermodynamic and kinetic factors, as well as those of the electronic properties on the catalytic performance of these complexes.

4.1. Thermodynamic considerations

Hydrogen activation is an important step in most catalytic cycles involving hydrogenation and dehydrogenation processes. The pincer system involving metal-ligand cooperation starts with the formation of the dearomatized complex. The hydrogen molecule (H_2) approaches the active site ($=\text{CH}\cdots\text{Metal}$ or $=\text{N}\cdots\text{Metal}$) driven by a van der Waals attractive force. The splitting of the H-H bond then occurs via a proton/hydride transfer process with the formation of the Metal-H hydride and a C-H or N-H bond. Recent studies on hydrogen activation by Wang and Huang *et al.* [74, 96] show completely different thermodynamic preferences between the Ru pincer complexes with $-\text{NPR}_2$ (**Ru16**) and $-\text{CHPR}_2$ (**MRu5**) arms (Figure 4(a) and 4(b)). The H_2 cleavage by **Ru16** is thermodynamically less favorable than that by the **MRu5** system. The former is endergonic by 2.7 kcal/mol, while the latter is exergonic by 10.0 kcal/mol. Changing the arm from a CH_2 spacer to the more acidic N-H spacer reverses the thermodynamic preference and thus may offer unusual properties, such as tolerating the presence of water. Kirchner and co-workers showed that H_2 activation by a dearomatized PN^3P -Fe complex is thermodynamically favored (Figure 4(c)), indicating that these properties are sensitively dependent on the metal center and auxiliary ligands [81].

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Figure 4. The free energy profile (kcal/mol) of intramolecular heterolytic dihydrogen cleavage by ruthenium and iron pincer complexes [74, 81, 96].

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4.2. Kinetic considerations

4.2.1. Activation energy barriers for H_2 activation. Apart from the thermodynamic differences discussed above, reaction kinetics is employed to compare the pincer systems with the $-CH_2$ arm and $-NH$ arms. It is characterized by a overstretched breaking H-H bond (1.11 Å) and a high energy barrier (TS2: 35.5 Kcal/mol) for the transition state of direct H_2 activation mediated by the PN^3 -Ru complex shown in Figure 4(b). Similarly, Huang and Wang *et al.* showed that the key energy barriers for dehydrogenation were up to 39.8 kcal/mol in the PN^3 -Ir system [74, 96]. The energy barriers for dehydrogenation were too high to be accessible under the experimental conditions. The CH spacer, however, had a much smaller energy barrier (**TS1**: 21.8 Kcal/mol).

Comparing **TS1** with **TS2** (Figure 5), a larger $\angle RuNH^1$ angle (52.5°) and a shorter N-H¹ bond

(1.33 Å) in **TS1** compared with the corresponding $\angle RuCH^1$ angle (50.9°) and C-H¹ bond (1.46 Å)

in **TS2** can be observed. The geometric variances do not seem large enough to be responsible for the difference in the activation energy barrier. A more reasonable comparison may be to look at the geometric distortion required to reach the preferred orbitals interactions between active sites.

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Figure 5. Optimized geometries of the transition states labeled in Figure 4. Key bond lengths and angles are given in angstroms and degrees, respectively. Trivial H atoms are omitted for clarity.

4.2.2. Molecular orbital analysis. The electronic structure, especially the frontier molecular orbital, is very important to the analysis of bond formation processes. The HOMO of the dearomatized Ir complex (**Ir3**) consists of the lone-pair of the imine arm perpendicular to the d_z^2 -like orbital of Ir. In contrast, the HOMO of the dearomatized Ru complex (**MRu5**) is the C=C π orbital perpendicular to the planar ligand framework. These observations suggest that the protonic $\text{H}^{\delta+}$ would prefer to attack the N of the **Ir3** and C of **MRu5** from different directions as

shown in Fig.6. The ideal “undistorted” $\angle \text{Ir-N-H}$ and $\angle \text{Ru-C-H}$ angles are thus 180° and 90° ,

respectively. Accordingly, the geometric deviations required for direct H_2 activation of **Ir3** and

MRu5 become 127.5° ($180^\circ - \angle \text{IrNH}^1$) and 39.1° ($180^\circ - \angle \text{RuCH}^1$), respectively, indicative of a

greater strain for the PN^3 system [96].

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Figure 6. (1A) HOMO of PNP-Ir (**Ir3**) and (2A) HOMO of Ru complex (**MRu5**) with focus on the active sites.

4.2.3. Proton-transfer shuttle. The energy barrier of direct H_2 activation in the PN^3 system is too high to be accessible. A reasonably low transition state barrier would require the $\text{H}^{\delta+}$ to reach the electron lone pair of N of the imine arm. Proton-transfer (H-transfer) shuttles were recently identified in facilitating various H-transfer processes in related reactions [58, 97-108]. The mediating agents for the H-transfer process can be protonic solvent molecules (alcohols and water), substrates, or products. In the PN^3 system, the one-water shuttle is not sufficient for hydrogen activation, while the two-water transfer shuttle can significantly lower the transition state energy barrier from 35.5 kcal/mol to an accessible value of 24.2 kcal/mol (**TS2_2W**). The

geometric distortion ($180^\circ - \angle \text{RuNH}^1$) also becomes much smaller (62.4°), compared with

127.5° in the direct hydrogen activation model. Such a proton-transfer shuttle is not necessary

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for H_2 activation in the PNN-Ru system (Figure 7). The transition state energy barrier remains approximately 25 kcal/mol even when a one-water shuttle is involved (**TS1_W**).

Figure 7. Free energy profile for H_2 activation via the proton-transfer (H-transfer) shuttles [74, 96].

4.3. Alcohol dehydrogenation via metal-ligand cooperation

The key steps of the proposed mechanism of the alcohol dehydrogenation by the dearomatized PNN-Ru pincer complex were considered to involve the β -H elimination from the Ru-alkoxide intermediate (the indirect dehydrogenation pathway) [42, 57]. Wang and co-workers have recently proposed an alternative straightforward pathway for alcohol dehydrogenation: bifunctional double hydrogen transfer (BDHT) [58]. This pathway transfers the two hydrogen atoms of alcohol to the metal-ligand bifunctional active sites in a concerted fashion. Further studies showed that the dehydrogenation reactions catalyzed by the Milstein catalyst favor the BDHT process rather than the β -H elimination mechanism. Both pathways for the PN^3 -Ir system were evaluated computationally (Figure 8). Either the hydrogen molecule elimination step or the dissociation of one of the phosphine arms was necessary to supply a vacant site on Ir for β -H elimination (**TS5** and **TS6**). The relatively large steric hindrance of the alcohol molecule to enter the inner coordination sphere of the catalyst suggests against the possibility of these paths. The first two steps can be achieved with low energy barriers using a H-transfer shuttle, but the β -H elimination rate-limiting step still requires very high energy (**TS7**:42.0 kcal/mol). Alcohol dehydrogenation catalyzed by the PN^3 -Ir pincer complex favors the BDHT pathway (Figure

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9). Direct BDHT in $\text{PN}^3\text{-Ir}$ gave the energy barrier of 32.5 kcal/mol (**TS8**), much lower than the overall energy barrier via $\beta\text{-H}$ elimination (**TS7**). When using one water and one alcohol molecule as the shuttle, the barriers can be further dropped to 24.6 (**TS8_W**) and 21.9 kcal/mol (**TS8_OL**), respectively.

Figure 8. The $\beta\text{-H}$ elimination pathway for $\text{PN}^3\text{-Ir}$ complex-catalyzed dehydrogenation of alcohol, along with the relative free energies [74, 96].

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Figure 9. The bifunctional double hydrogen transfer (BDHT) dehydrogenation pathway for PN^3 -Ir complex-catalyzed dehydrogenation of alcohol, along with the relative free energies [74, 96].

4.4. Hydrogenation of esters via metal-ligand cooperation

The previous mechanism for alcohol dehydrogenation is applicable to the PN^3 -Ru system. Using the hydrogenation of ethyl acetate to ethanol as an example, this reaction proceeds via hydrogen activation (**TS9**), hydrogen transfer (**TS10**), proton transfer (**TS11** and **TS12**) and aldehyde hydrogenation (**TS13**) steps (Figure 10) [74]. As discussed above, the two-water transfer shuttle is crucial to reducing the key barriers to the experimentally accessible values. Experimental studies at low reaction conversions supported the formation of aldehyde intermediates that were hydrogenated to the corresponding alcohols at a faster rate than those for the ester starting materials.

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Figure 10. A computed mechanism for the hydrogenation of ethyl acetate to ethanol catalyzed by **Ru16** [74, 96].

5. Conclusion and future prospects

Synthetic methods for preparing various PN³-pincer ligands have been developed using readily available starting materials. The complexation of these ligands with transition metals is straightforward, allowing convenient access to the corresponding pincer complexes with easily modifiable steric and electronic properties. The coordination chemistry of transition metal complexes has been investigated using Cr, Ir, Ni, Cu, Mo, Ru, Pd, W, Ir, and Au. Rich reactivities have been observed with their catalytic activities being explored recently. In very recent work, we have witnessed that the seemingly small change by replacing the CH₂ spacer in the pyridine-based pincer complex with an NH group has dramatically influenced the thermodynamic and kinetic properties, and in some cases the catalytic behaviors of the corresponding metal complexes. It is conceivable that this new class of transition metal pincer complexes will offer exciting opportunities for the discovery of other unprecedented reactivities for the development of novel catalytic applications.

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Review

A New Class of PN^3 -Pincer Ligands for Metal-Ligand Cooperative Catalysis

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Highlights:

- Introduction of PN^3 -pincer ligands for metal-ligand cooperative catalysis
- Preparation and coordination chemistry of PN^3 -pincer ligands
- Focus review on the role of dearomatization-rearomatization processes
- Mechanistic insights from DFT calculations for thermodynamic and kinetic considerations.