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Metal–Ligand Cooperation

System with Potential Dual Modes of Metal–Ligand Cooperation: Highly Catalytically Active Pyridine-Based PNNH–Ru Pincer Complexes

Eran Fogler,^[a] Jai Anand Garg,^[a] Peng Hu,^[a] Gregory Leitus,^[b] Linda J. W. Shimon,^[b] and David Milstein^{*[a]}

Abstract: Metal–ligand cooperation (MLC) plays an important role in catalysis. Systems reported so far are generally based on a single mode of MLC. We report here a system with potential for MLC by both amine–amide and aromatization–dearomatization ligand transformations, based on a new class of phosphino–pyridyl ruthenium pincer complexes, bearing *sec*-amine coordination. These pincer complexes are effective catalysts under unprecedented mild conditions for acceptorless dehydrogenative coupling of alcohols to esters at 35 °C and hydrogenation of esters at room temperature and 5 atm H₂. The likely actual catalyst, a novel, crystallographically characterized monoanionic de-aromatized enamido–Ru^{II} complex, was obtained by deprotonation of both the N–H and the methylene proton of the N-arm of the pincer ligand.

Metal–ligand cooperation (MLC), in which both the metal and the ligand undergo bond-making and breaking with incoming substrates, plays an important role in catalysis.^[1] A prevailing mode of MLC, pioneered catalytically by Noyori^[1a–d] and stoichiometrically by Fryzuk,^[2] is based on metal cooperation with ligands bearing N–H groups, mostly of the form H–M–NHR (Figure 1 a).^[1] Among several systems that operate in this fashion, pincer-type ligands have recently shown exceptional catalytic activity in hydrogenation and dehydrogenation reactions involving carbonyl groups.

Examples of catalytic reactions based on metal–amine/metal–amide MLC (Figure 1 a) include catalytic hydrogenation of aldehydes, esters,^[4a,b,5d–f] imines, ketones,^[1e,4c,5] nitriles,^[6] amides,^[7a,b] and even cyclic carbonates.^[7c] Dehydrogenative coupling of alcohols to esters,^[5c] alcohols with amines to form ami-

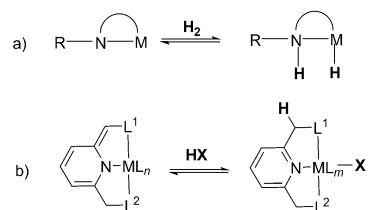


Figure 1. MLC in a) amine–amide ligands and b) aromatization–dearomatization of pyridine-based ligands.

des,^[7b,8] as well as other catalytic reactions were also reported.^[11,9]

We have developed a new mode of MLC, involving aromatization/dearomatization of pyridine- and bipyridine-based ligands. For example, deprotonation of the benzylic proton α to the pyridine group can lead to its dearomatization. The dearomatized moiety can regain its aromaticity by cooperation between the metal and the ligand, resulting in the activation of chemical bonds, such as H–X (X = NR₂, H, OR or C), without formal change in the metal oxidation state (Figure 1 b).^[3] PNN–Ru pincer complexes used in such MLC are shown in Figure 2.

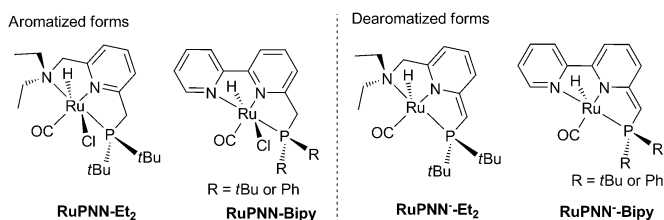


Figure 2. Examples of Ru^{II} pincer complexes used in aromatization–dearomatization based MLC

Several new, environmentally benign reactions catalyzed by PNP or PNN/Ru or Fe pincer complexes, based on an aromatization/dearomatization strategy have been developed. They include dehydrogenative coupling of alcohols to esters, hydrogenation of esters to alcohols, coupling of alcohols with primary amines to form amides with liberation of H₂, direct synthesis of imines from alcohols and amines with liberation of H₂, catalytic coupling of nitriles with amines to selectively form imines, and several other catalytic transformations.^[3] We were intrigued by the possibility that combining both prevailing MLC modes in

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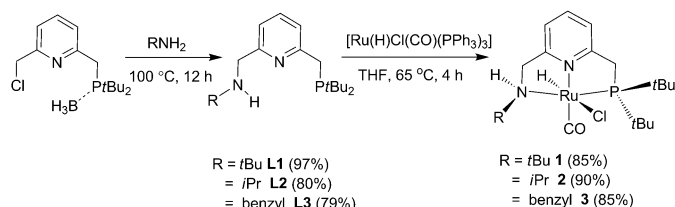
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one complex might lead to enhanced catalytic activity, due to the ability of the complex to “choose” the MLC path with the lowest activation energy in each stage of the catalytic cycle.

Three PNN–H ligands bearing different substituents [R = *tert*-butyl (**L1**), isopropyl (**L2**), and benzyl (**L3**)] were synthesized by reaction of 2-(ClCH₂)-6-[*t*Bu₂P(BH₃)CH₂]-C₆H₄N^[11] with the corresponding amines (Scheme 1). The corresponding ruthenium



Scheme 1. Synthesis of PNN–H ligands and their corresponding Ru^{II} complexes (see Supporting Information).

complexes were obtained in 85–90% yields by reacting the ligands with [Ru(H)Cl(CO)(PPh₃)₃] (Scheme 1).

The fully characterized complexes **1–3** give rise to a singlet around 109.0 ppm in the ³¹P{¹H} NMR spectra. In ¹H NMR spectra, the hydride bound to Ru appears as a doublet around –15.0 ppm (*J*_{HP} ca. 13.0 Hz). The inequivalent geminal benzylic methylene protons attached to phosphorus appear in all cases as a doublet-of-doubles around 3.5 ppm and 3.42 ppm.

The methylene protons attached to the N atom resonate further downfield in the region 4.7–4.3 ppm. The carbonyl carbon in the ¹³C{¹H} NMR spectrum exhibits the most downfield shift, resonating around 208.0 ppm (*J*_{CP} ca. 16.0 Hz) with a characteristic doublet. In the IR spectra, the carbonyl group absorbs in the range $\nu(\text{CO}) = 1898\text{--}1896\text{ cm}^{-1}$, indicating a slightly higher back-bonding than in the analogous complex **RuPNN–Et₂** ($\nu(\text{CO}) = 1901\text{ cm}^{-1}$) previously reported.^[10a]

Single crystals suitable for X-ray diffraction of complexes **1–3** were obtained by slow diffusion of pentane into solutions of the complexes in CH₂Cl₂. Similar to the structure of **RuPNN–Et₂**,^[10a] these complexes exhibit a distorted meridional octahedral structure with phosphorus, carbonyl, and chloride atoms

trans to the amine nitrogen, pyridine, and hydride respectively. In all cases the substituents attached to the nitrogen atoms are equatorially disposed due to the steric hindrance on either side of the N1–Ru–N2 plane. Perspective views of the complexes are shown in Figure 3. Compared to **RuPNN–Et₂**, the distances of the chelating atoms to the metal are similar except for the significantly shorter Ru–NHR distance (by ca. 0.5 Å), indicating that the *sec*-amine ligands are bound significantly more strongly. These distances are in the range reported for the *sec*-amine coordinated pincer complex [Ru{2-(*i*Pr₂PC₂H₄NHCH₂)C₆H₄N}]^[5d].

Next, we explored the reactivity of **1** with a base. We have previously observed that with the analogous **RuPNN–Et₂** complex, addition of an equivalent of base leads to deprotonation of the benzylic phosphine arm, with concomitant dearomatization of the pyridine-based pincer group. In the case of the *sec*-amine complex **1**, in which the coordinated amine group is expected to be less basic (compared with non-coordinated amine), competition between the benzylic arm and the N–H group is expected.

Addition of 1.2 equivalents of either potassium bis(trimethylsilyl)amide (KHMDs) or potassium *tert*-butoxide (KO^{*t*}Bu) to **1** in THF at RT leads to two signals at 98.0 and 93.0 ppm in the ³¹P{¹H} NMR spectrum, with complete disappearance of the starting material. However, isolation of the products from the mixture was unsuccessful. It was observed that with time the intensity of both the signals in the reaction mixture decreased, leading to a violet precipitate from an initially brown solution. The same phenomenon was seen upon incremental addition of base from 0.5 to 2.2 equivalents (see the Supporting Information, Figures S1 and S2), the overall addition being complete in 1.0 h. Surprisingly, the violet product thus obtained with either 1.1 or 2.2 equivalents of base was not observable in the ³¹P{¹H} NMR and ¹H NMR spectra at room temperature. However, when **1** was reacted with 2.2 equivalents of KHMDs in a NMR tube at room temperature and then cooled to –40 °C, it showed a new broad signal at 124.0 ppm in ³¹P{¹H} NMR spectrum with a corresponding hydride signal at –18.5 ppm in the ¹H NMR spectrum (see the Supporting Information, Figure S3A). These signals were tentatively assigned to the anionic complex resulting from deprotonation of both the

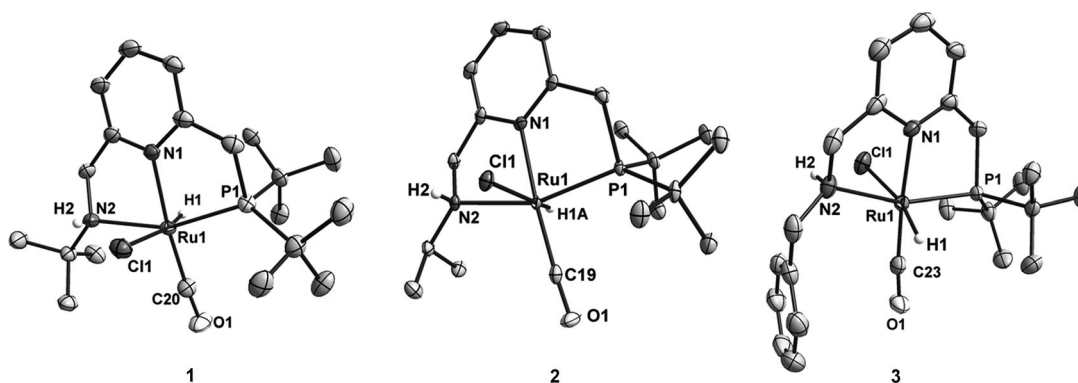


Figure 3. X-ray structure of complexes **1–3**. Hydrogen atoms (except for the hydride and amine hydrogen) are omitted for clarity. Selected bond lengths/angles are provided in the Supporting Information (Table S1).

amine and one of the methylene protons, even though the broadness of the signal precluded complete NMR characterization. However, the mass (ES^+) spectrum recorded for this air-sensitive violet product matched with that of the expected anionic complex (see the Supporting Information, Figure S3B). Fortunately, violet crystals suitable for X-ray diffraction were obtained from a mixture of THF/diethyl ether. As expected, it revealed a double-deprotonated enamido monoanionic complex with K^+ as counterion, forming a distorted square-pyramidal geometry with the hydride located at the apical position (Figure 4). Interestingly, in contrast to the deprotonation of the

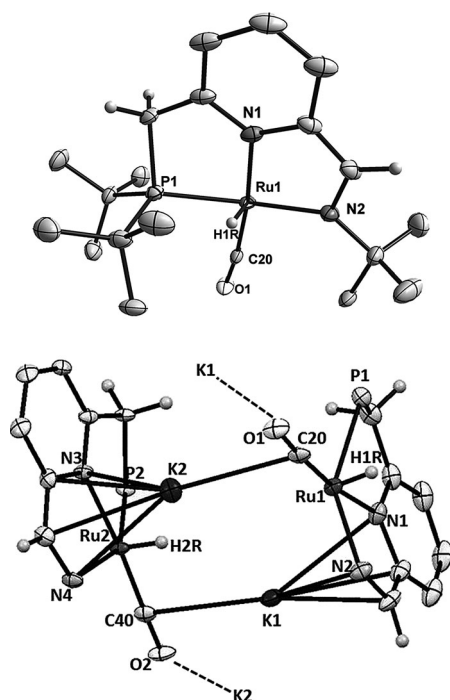
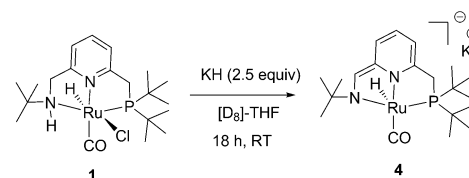


Figure 4. Top: X-ray structure of complex **4**. Selected hydrogen atoms and K^+ are omitted for clarity. Bottom: Section of the unit cell showing connections with K^+ . Substituents on phosphorus and nitrogen are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Ru1–H1R 0.95(5); Ru1–C20 1.816(4); Ru1–N1 2.061(3); Ru1–N2 2.063(3); Ru1–P1 2.2581(10); N1–Ru1–H1R 82(3); N2–Ru1–H1R 89(2); N2–Ru1–P1 145.71(10); N1–Ru1–C20 173.26(15).

P-arm methylene protons, as previously observed in the dearomatized forms of **RuPNN-Et₂**,^[10a] C–H deprotonation took place on the N-arm, as clearly indicated by the short Csp²–Csp³ bond length of 1.371 Å of the N-arm and the presence of only one C–H bond. In addition, the absence of a proton attached to nitrogen unequivocally indicates that double deprotonation took place. The other bond lengths fall in the expected ranges. The molecular packing shows two successively independent Ru pincer molecules disposed roughly at 120° to each other, connected by potassium ions, bridging the deprotonated amine arm and the carbonyl carbon.

Experiments involving addition of base at low temperature and monitoring the progress by VT-NMR spectroscopy suggested formation of the dearomatized complex as the first formed intermediate, observed at 98.0 ppm in the ³¹P NMR



Scheme 2. Preparation of the monoanionic complex **4** by double deprotonation of **1**

spectrum (see the Supporting Information, Scheme S1). Finally, reaction of **1** with KH (2.5 equiv) in THF at room temperature resulted in formation of the violet enamido anionic complex **4** within 18 h (Scheme 2)

Monitoring the progress of the reaction at early intervals reveals the same set of intermediates, namely the dearomatized intermediate and the amido intermediate, finally leading to the violet precipitate, showing a singlet in the ³¹P{¹H} NMR spectrum at 124.0 ppm and hydride at –18.5 ppm in the ¹H NMR spectrum (see the Supporting Information, Figure S5). A glance at the ¹H NMR reveals that the aromatic ring protons have shifted upfield (to 5.0–6.2 ppm) due to the dearomatization. The enamino proton resonates most downfield at 6.6 ppm (see the Supporting Information, Figure S6 A).

Acceptorless catalytic dehydrogenative coupling of alcohols and hydrogenation of esters are of particular interest.^[1u, 3, 5, 10, 11] Our initial catalytic experiments with the hydridochloride complexes **1–3** in the presence of varying equivalents of base indi-

Table 1. Acceptorless dehydrogenative coupling of primary alcohols at 35 °C with diethylether as solvent.^[a]

$2R-OH \xrightarrow[\text{Et}_2\text{O reflux open system}]{\text{catalyst (0.1 mol\%) KOtBu (0.22 mol\%)}} R-O-C(=O)-R + 2H_2 \uparrow$					
Alcohol	Ester	Catalyst	t [h]	Yield [%]	
1		RuPNN-Et₂	40	< 1	
		RuPNN-Bipy	40	< 1	
		3	40	37	
		3	144	57	
2		3	40	56	
3		3	15	41	
		3	96	97	
4		3	40	60	
5		3	40	72	
6		3	40	41	
		3	144	97	
7		3	40	95	

[a] Reaction conditions: substrate (5.0 mmol), catalyst (0.1 mol%), KOtBu (0.22 mol%), diethyl ether (3.0 mL), bath temperature 45 °C, open system under Ar flow with cold water circulation. Yields were determined by GC, *m*-xylene was used as internal standard.

cated that they are superior catalysts to **RuPNN-Et₂** or **RuPNN-Bipy** (reported previously)^[10a,e] for dehydrogenative coupling of alcohols under mild conditions of benzene reflux. Thus, refluxing a solution of 1-hexanol in benzene with 0.1 mol% complex **3** and 0.22 mol% KOtBu resulted in 97% yield of hexyl hexanoate after one hour. On the other hand, the same experiment using **RuPNN-Et₂** as catalyst resulted in only 2% yield of hexyl hexanoate after one hour. Typically, in our earlier work, good conversions were achieved at the higher temperature of toluene reflux.^[10a] Further, optimization experiments (Table S2, Supporting Information) with **1**, indicated that the best catalytic activity is achieved by the use of 2.2 equivalents of base with respect to the catalyst. This observation is in line with the in situ, quantitative generation of the double-deprotonated anionic complex that is primarily responsible for the higher catalytic activity. All the three complexes **1–3** showed similar superior activity for dehydrogenative esterification reactions (Tables S2, Supporting Information). As expected, the isolated monoanionic enamido complex **4** was also an excellent catalyst for the dehydrogenative coupling of alcohols to esters. Thus, conversion of 1-hexanol to hexyl hexanoate reached completion in one hour under toluene reflux without the need of base (Table S2, entry 8, Supporting Information). Among the pre-catalysts, the reactivity order was **3** > **2** > **1** (Table S2, entries 4–6, Supporting Information). Employing the *N*-benzyl complex **3** as the pre-catalyst under the optimized conditions (0.1 mol% complex and 0.22 mol% of base), we explored the possibility of unprecedented, near-room-temperature conditions for dehydrogenative coupling of alcohols. Encouragingly, **3** catalyzed dehydrogenative coupling of benzyl alcohol to form benzyl benzoate even in refluxing diethyl ether (b.p. 35 °C) as solvent. While **RuPNN-Et₂** and **RuPNN-Bipy** showed less than 1% conversion at this low temperature, catalyst **3** yielded 37% of benzyl benzoate at the end of 40 h (Table 1). Hexyl hexanoate was quantitatively obtained after 96 h and 2-methoxyethanol required six days for near quantitative conversion in diethyl ether reflux. Conversion of the electron deficient 2,2,2-trifluoroethanol proceeded smoothly giving 95% yield in 40 h. Linear branched alcohols such as 2-methylbutanol also furnished 72% yield of corresponding ester at the end of 40 h. Vigorous reflux under

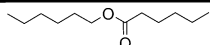
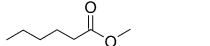
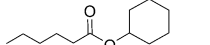


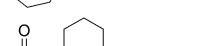
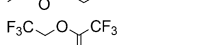

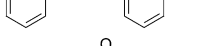
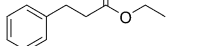
the flow of argon to drive out the H₂ generated was found to be critical for the success of these experiments.

Next, we aimed at the hydrogenation of esters at the very mild conditions of 5.0 bar H₂ pressure and room temperature. Gratifyingly, **3** (0.5 mol%) efficiently catalyzes the hydrogenation of hexyl hexanoate to 1-hexanol in quantitative yield at RT after 24 h (Table 2). Esters such as methyl hexanoate and cyclohexyl hexanoate (Table 2, entries 2 and 3) were converted to their respective alcohols in quantitative yields. ϵ -Caprolactone was also smoothly hydrogenated to hexane-1,6-diol. Here again, 2.2 equivalents (1.1 mol%) of KOtBu was found to be enough for achieving high conversions. However, with **1** as catalyst, using 10.0 equivalents of base was beneficial (Table 2, entries 6, 9, and 10).

These catalysts also showed high efficiency in loadings as low as 0.02 mol% and with 1.1 mol% of base at room temperature, but with a higher H₂ pressure of 50 bar (Table S3, Supporting Information, entry 3).

In summary, a novel system with potential for dual-mode MLC was developed. Ru complexes bearing pyridine-based PNNH-type pincer ligands, capable of MLC by ligand amine–amide as well as aromatization–dearomatization modes, were prepared. In the presence of 2.2 equivalents of base (relative to Ru), these complexes catalyze the acceptorless dehydrogenative coupling of alcohols, and hydrogenation of esters, under

Table 2. Hydrogenation of esters at room temperature and 5 atm.^[a]

$\text{R}-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{R}' \xrightarrow[\text{5 bar H}_2]{\text{1 or 3 (0.5 mol\%)}, \text{KOtBu, THF, RT (19–24 } ^\circ\text{C)}} \text{R}-\text{CH}_2-\text{OH} + \text{R}'-\text{CH}_2-\text{OH}$						
Reactant	Catalyst	t [h]	Base [mol%]	Conv [%]	Product, yield [%]	
1 	3	24	1.1	99	1-hexanol, 99	
2 ^[b] 	3	24	1.1	99	1-hexanol, 99	
3 	3	24	1.1	99	cyclohexanol, 98; 1-hexanol, 98	
4 ^[b] 	3	24	1.1	99	tert-butanol, 99	
5 	3	24	1.1	99	hexane-1,6-diol, 98	
6 ^[b] 	1	24	5.0	93	cyclohexanol, 93	
7 ^[b] 	3	32	1.1	80	2,2,2-trifluoroethanol, 74	
8 	3	24	1.1	77	benzyl alcohol, 75	
9 ^[b] 	1	24	5.0	96	3-phenylpropan-1-ol, 91	
10 ^[b] 	1	48	5.0	88	benzyl alcohol, 83	

[a] Reaction conditions: substrate (1.0 mmol), THF (1.0 mL), room temperature 19–24 °C. Yields were determined by GC with an internal standard. [b] Yields of methanol, ethanol and trifluoromethanol are not reported.

exceedingly mild conditions. A novel anionic, double deprotonated, dearomatized enamido Ru^{II} complex, generated in situ in these reactions, was prepared and characterized by X-ray crystallography. Mechanistic studies are underway. We believe that this work provides a new approach to catalytic design by metal complexes.

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Keywords: dehydrogenation • hydrogenation • metal–ligand cooperation • pincer complex • ruthenium

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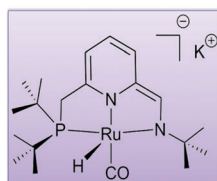
COMMUNICATION

Metal–Ligand Cooperation

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 **System with Potential Dual Modes of Metal–Ligand Cooperation: Highly Catalytically Active Pyridine-Based PNNH–Ru Pincer Complexes**



Novel anionic, dearomatized, amido Ru^{II} pincer complex.

Catalysis under exceedingly mild conditions:

- ❖ *Acceptorless dehydrogenative coupling of alcohols at 35 °C*
- ❖ *Hydrogenation of esters at ambient temperatures and 5.0 atm.*

Cooperation with a pinch! Ruthenium complexes with potential for dual-modes of metal–ligand cooperation, involving amine–amide and aromatization–dearomatization modes, catalyze dehydrogenative coupling of primary al-

cohols and hydrogenation of esters under previously unseen mild conditions. Deprotonation of such a complex has led to a novel monoanionic dearomatized complex.