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PNN Ruthenium Pincer Complexes Based on Phosphinated 2,2′-Dipyridinemethane and 2,2′-Oxobispyridine. Metal−Ligand Cooperation in Cyclometalation and Catalysis

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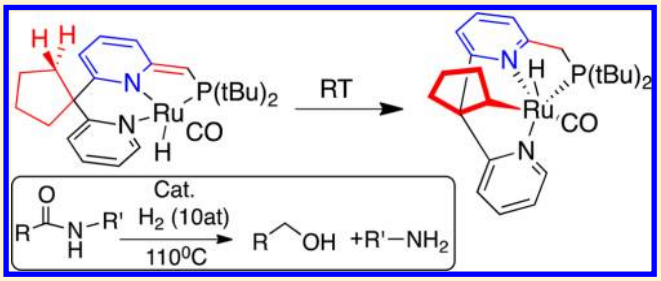
Supporting Information

ABSTRACT: The synthesis of novel PNN ruthenium pincer complexes based on 2,2′-dipyridinemethane phosphine derivatives, as well as on 2,2′-oxobispyridine phosphine ligands, and their reactivity toward dearomatization and cyclometalation are described. The dearomatized compounds **7a**,**b** undergo cyclometalation to yield complexes **8a**,**b**. In order for cyclometalation to proceed, the coordination sphere around the Ru center has to rearrange, and this depends on the flexibility of the system, showing that the cyclometalation is qualitatively faster in the case of the dimethyl derivative **7a** than in the case of the spyrocyclopentyl derivative **7b**. The cyclometalation occurs diastereoselectively and leads to only one diastereomer of the cyclometalated compounds. In the case of the 2,2′-oxobispyridine complex **6c**, the dearomatized complex was too unstable to be isolated; however it was possible to isolate and characterize a stable dicarbonyl-dearomatized ruthenium(II) complex, **9c**, when the deprotonation was performed under a CO atmosphere. Dearomatization of **6a** under CO also led to dicarbonyl-dearomatized ruthenium(II) complex **9a**, which slowly rearranged into the dicarbonyl-aromatized ruthenium(0) complex **10a**. These complexes were tested in catalytic alcohol−amine coupling, esterification of primary alcohols, and hydrogenation of secondary amides. Moderate activity was observed in hydrogenation of amides to alcohols and amines and low activity in the other transformations, owing mainly to the formation of stable cyclometalated compounds.



INTRODUCTION

Our group has developed a new mode of metal−ligand cooperation involving dearomatization/aromatization of pyridine-based PNN and PNP pincer complexes, which were employed in the activation of C−H,[1] O−H,[2] N−H,[3] and H−H[4] bonds and in catalytic, environmentally friendly organic transformations.[5] Among these complexes, the bipyridine-based pincer complex **1** (Figure 1), which exhibits excellent catalytic activity, such as in the hydrogenation of secondary amides to alcohols and amines,[4b] hydrogenation of urea derivatives[4c] and carbamates[4e] into amines and methanol, hydrogenation of organic carbonates, formates, and biomass derived cyclic diesters,[4i] the synthesis of polyamides by direct coupling of diols and diamines,[2m] and the synthesis of peptides[2f] and pyrroles[2n] from amino alcohols.

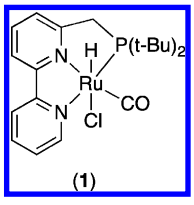


Figure 1. Complex **1**.

In continuation of this work, we have now synthesized novel, more flexible, expanded PNN-type pincer ruthenium complexes. These complexes undergo dearomatization upon deprotonation, followed by an unusual cyclometalation reaction, involving metal−ligand cooperation, resulting in rearomatization, with retention of the metal oxidation state. These complexes were also evaluated as catalysts in the coupling of alcohols with amines, dehydrogenation of alcohols to esters, and hydrogenation of secondary amides. Cyclometalated compounds[6,7] have been utilized in organic synthesis,[6a,b] catalysis,[8] asymmetric synthesis,[6g] and photochemistry.[6h,i]

RESULTS AND DISCUSSION

Synthesis of 2,2′-Dibipyridinemethane-Based PNN Ligands. Ligands **2a** and **2b** were prepared according to Scheme 1. Reaction of 2,6-lutidine with 2-fluoropyridine and *n*-BuLi in THF resulted in the methyl bipyridinemethane

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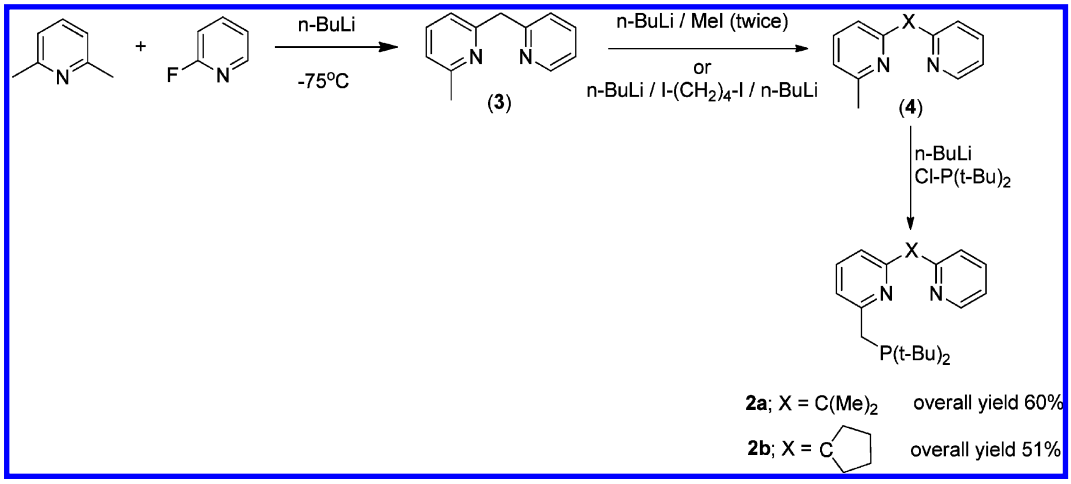
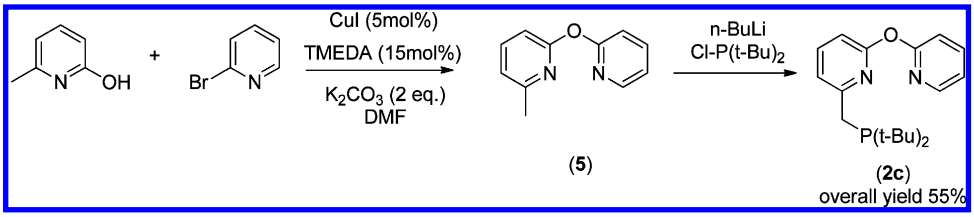
Scheme 1



Scheme 2

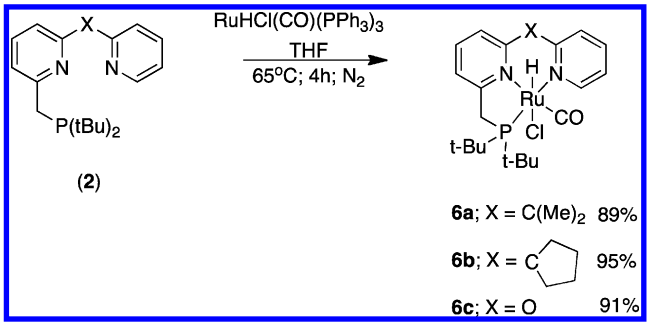


compound **3**. Alkylation of the bridging methylene group was performed by deprotonation with *n*-BuLi and dropwise addition of a slight excess of iodomethane in THF two times, to obtain **4a**, or 1,4-diiodobuthane in an intramolecular process to give compound **4b**. Phosphination of **4a**,**b** took place by using a slight excess of *n*-BuLi and ClP(*t*-Bu)$_2$ to obtain ligands **2a** and **2b**.

Ligand **2c**, bearing a bridging oxygen atom, was prepared using the methodology reported by Buchwald[9] for the coupling of 6-methyl-2-hydroxypyridine and 2-bromopyridine in the presence of a catalytic amount of CuI in DMF to give the oxobispyridine compound **5** in good yield. Reaction of **5** with a slight excess of *n*-BuLi and ClP(*t*-Bu)$_2$ resulted in ligand **2c** (Scheme 2).

Synthesis of PNN-RuHCl(CO) Complexes. The PNN-Ru complexes **6a**−**c** were prepared following the methodology described in the literature for the corresponding bipyridyl-phosphine derivatives, by reacting the [RuHCl(CO)(PPh$_3$)$_3$] precursor with a slight excess of the electron-rich PNN ligands **2a**−**c** in THF at 65 °C for 4 h under a N$_2$ atmosphere (Scheme 3).[4b]

Scheme 3



Complexes **6a**−**c** were the single products of each reaction. Table 1 summarizes the characteristic signals in multinuclear NMR of each complex.

Table 1[a]

complex	^{31}P NMR	^{1}H NMR (hydride)	^{1}H NMR (methylene arm)	^{13}C NMR (CO)
6a	108.5 (s)	−14.5 (d, $^{2}J_{PH}$ = 26.1 Hz)	4.1 (dd, J_{PH} = 7.8 Hz, J_{HH} = 16.5 Hz) 3.6 (dd, J_{PH} = 12.0 Hz, J_{HH} = 16.8 Hz)	207.1 (d, J_{PC} = 17.7 Hz)
6b	108.9 (s)	−14.5 (d, $^{2}J_{PH}$ = 26.1 Hz)	4.1 (dd, J_{PH} = 7.8 Hz, J_{HH} = 16.8 Hz) 3.6 (dd, J_{PH} = 11.7 Hz, J_{HH} = 17.1 Hz)	207.2 (d, J_{PC} = 17.4 Hz)
6c	112.8 (s)	−14.5 (d, $^{2}J_{PH}$ = 23.6 Hz)	3.8 (dd, J_{PH} = 8.9 Hz, J_{HH} = 16.2 Hz) 3.4 (dd, J_{PH} = 10.4 Hz, J_{HH} = 16.1 Hz)	206.4 (d, J_{PC} = 17.2 Hz)

[a]NMR experiments were recorded at room temperature using CD_2Cl_2 as solvent. Chemical shifts are given in ppm.

There are no significant differences between the NMR spectra of complexes **6a**−**c**, and the chemical shifts of these complexes are quite similar to the previously reported complex **1**.[4b] Structures of complexes **6a** and **6b** were also confirmed by single-crystal X-ray diffraction studies. These complexes display distorted octahedral geometries around the ruthenium center with the PNN pincer ligand coordinated in a meridional fashion, the CO ligand being located *trans* to the central pyridine nitrogen, and the hydride *trans* to chloride (Figure 2).

Dearomatization Reactions. Upon treatment of complex **6a** with a slight excess of *t*-BuOK in THF at −35 °C, a dark green solution was obtained. The ^{1}H NMR spectrum of the reaction mixture at room temperature in benzene-d_6 revealed the presence of two new hydride complexes. One complex

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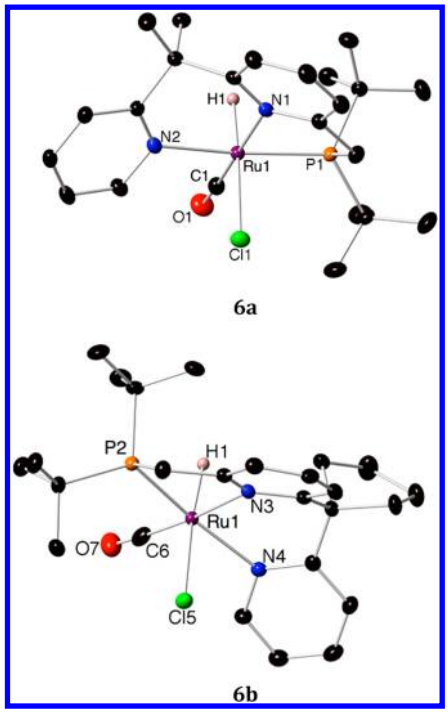


Figure 2. ORTEP drawing of PNN-Ru complexes **6a** and **6b** at 50% probability. Hydrogen atoms (except hydride) are omitted for clarity.

exhibited the presence of a hydride ligand as a doublet at −22.1 ppm ($^2J_{PH}$ = 29.1 Hz) and a phosphine singlet at 102.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum, corresponding to the expected dearomatized complex **7a**. The second complex, **8a**, exhibited a hydride signal as a doublet at −12.1 ppm ($^2J_{PH}$ = 20.4 Hz) and a phosphine singlet at 108.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Compound **8a** was obtained as the sole product of this reaction after 4 h at −35 °C. Upon workup, **8a** was characterized as the cyclometalated complex, which was formed by C−H activation of one of the methyl groups between the pyridine rings in the dearomatized complex **7a** (Scheme 4).

Upon treatment of complex **6a** with KHMDS (potassium hexamethyldisilazide) at −35 °C in toluene-d_8 in an NMR tube, the dearomatized compound **7a** was observed as the sole product. Upon warming to room temperature, **7a** transformed to the cyclometalated RuH complex **8a**, indicating that **7a** is an intermediate in the formation of **8a**.

This type of cyclometalation via metal−ligand cooperation is uncommon. It involves intramolecular diastereoselective C−H activation, with aromatization of the pyridine moiety and no change in metal oxidation state. Intermolecular C−H activation by metal−ligand cooperation, involving aromatizaion of pincer ligands, has been reported by our group.[1]

Crystals of complex **8a** suitable for X-ray diffraction were grown from a saturated benzene solution. The geometry around the ruthenium center is a highly distorted octahedron with the PNC system coordinated in a pseudomeridional fashion, the terminal pyridine ring occupies the apical position *trans* to hydride, and the CO is coordinated *trans* to the nitrogen of the central pyridine ring (Figure 3).

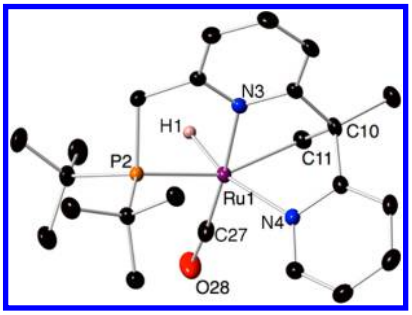


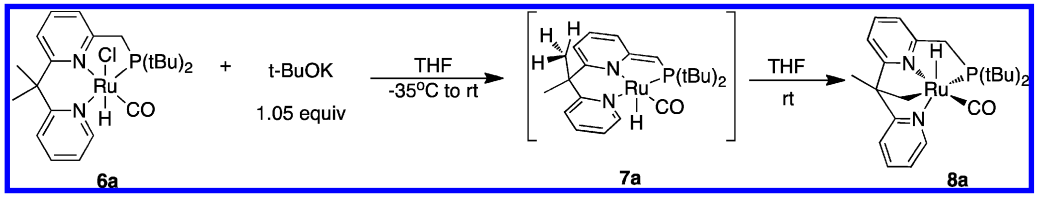
Figure 3. ORTEP drawing of PNN-Ru complex **8a** at 50% probability. Hydrogen atoms (except hydride) are omitted for clarity. Selected bond distances (Å): Ru1−C27 1.823(2), Ru1−N3 2.1014(15), Ru1−C11 2.1369(19), Ru1−N4 2.2325(16), Ru1−P2 2.3321(5), Ru1−H1 1.58(2). Selected angles (deg): C27−Ru1−N3 175.52(8), C27−Ru1−C11 104.68(8), N3−Ru1−C11 76.80(7), C27−Ru1−N4 100.97(8), N3−Ru1−N4 83.49(6), C11−Ru1−N4 74.72(7), C27−Ru1−P2 96.67(6), N3−Ru1−P2 81.13(4), C11−Ru1−P2 156.08(5), N4−Ru1−P2 111.98(4), C27−Ru1−H1 87.2(9), N3−Ru1−H1 88.6(9), C11−Ru1−H1 90.0(9), N4−Ru1−H1 164.0(9), P2−Ru1−H1 80.3(9).

Significantly, only one diastereoisomer of complex **8a** was formed, as indicated by the ^1H and $^{31}P\{^1H\}$ NMR spectra. The chirality in the complex is conferred by the chiral Ru1 and C10 centers in the complex. Complex **8a** has very low solubility in most of the common solvents (benzene, toluene, THF, acetone, and MeOH). It is very stable and unreactive in these solvents even at high temperatures or in the solid state (up to 130 °C).

Complex **6b** is expected to have a lower tendency toward cyclometalation since it is more difficult for a C−H bond of the spirocyclopentyl group to approach the metal center. In this case, unlike the case of **7a**, the dearomatized compound **7b** was isolated as a single product, and it was stable in solution at room temperature for several hours; nevertheless, conversion to the cyclometalated product **8b** was observed after 2 days and was complete at room temperature after 5 days, forming **8b** as a single product (Scheme 5).

Cyclometalation of complex **7b** is slower than that of the dimethyl analogue **7a** (which formed the cyclometalated compound after 4 h, as described above). Figure 4 shows ^1H NMR follow-up of this transformation, expanded in the hydride region. It is remarkable that only one diastereomer is formed along the reaction (on the basis of ^1H and ^{31}P NMR), despite the formation of three chiral centers. Interestingly complex **8b** is soluble in common solvents, unlike the very insoluble **8a**.

Scheme 4



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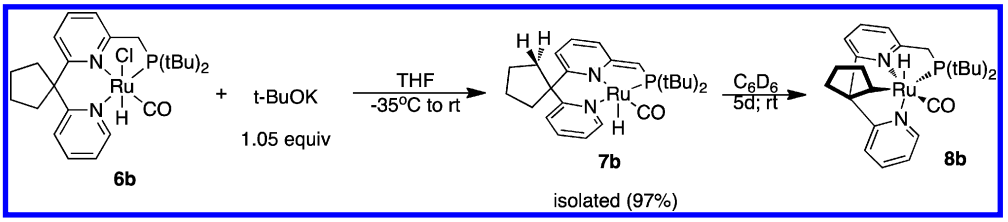
Scheme 5



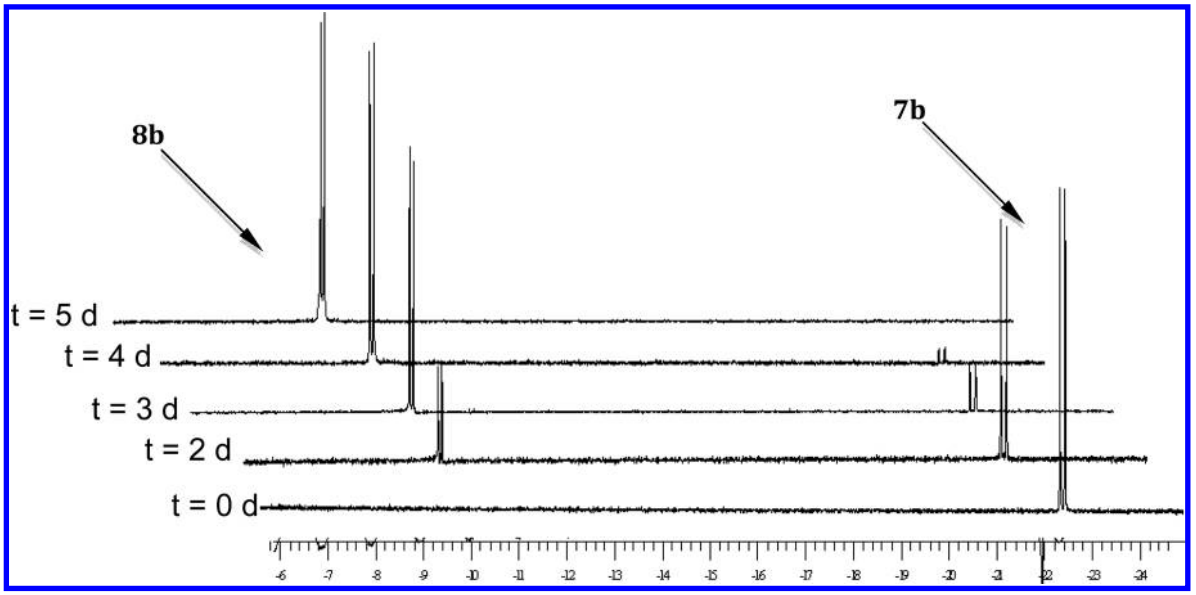
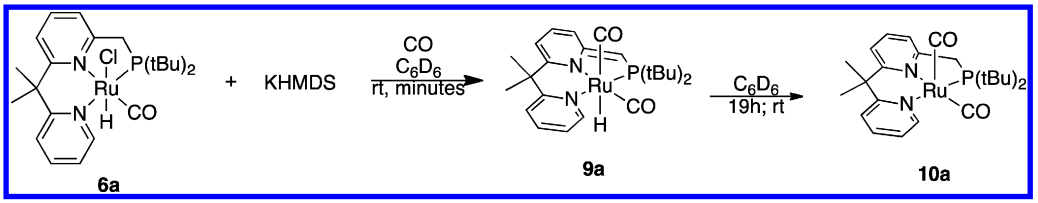


Figure 4. ^{1}H NMR follow-up of the cyclometalation of **7b** in benzene-d_6 showing the hydride region.

Scheme 6



Similar treatment of the oxygen-bridged complex **6c** with 1.02 equivalents of *t*-BuOK in THF at −35 °C led to a mixture of unidentified compounds. Several attempts to obtain the expected dearomatized compound were performed, including use of less polar solvents such as toluene or benzene or using KHMDS as the base, but mixtures of several unidentified products were obtained. The low stability of the expected dearomatized compound could be attributed to the presence of the donor oxygen atom directly linked to the pyridine rings, which increases the electron density of these ligands and destabilizes the deprotonated complex.

Dearomatization Reaction in the Presence of CO and Formation of Ru(0) Complexes. Upon deprotonation of complex **6a** in the presence of CO, the dearomatized PNN-Ru(II) complex **9a** was formed as a single product. The ^{1}H NMR spectrum of the dearomatized compound exhibits the hydride ligand at −4.3 ppm (d, $^2J_{HP}$ = 18.8 Hz), downfield from the chemial shift of the hydride of complex **6a** (−22.1 ppm), which is consistent with coordination of a CO ligand *trans* to the hydride. Methyl and *tert*-butyl groups in complex **9a** are diastereotopic, indicating a *cis* coordination of the CO groups in the Ru center. Significantly, the methyl groups of the ligand remained unreactive and did not undergo cyclometalation, indicating that an unsaturated metal center is required for cyclometalation, as expected. Interestingly, after 19 h at room temperature the dicarbonyl dearomatized Ru(II) complex **9a** underwent rearrangement to the PNN-Ru(0) complex **10a**. The presence of two diastereomeric methyl groups in ^{1}H NMR confirmed the *cis* coordination of the two CO ligands in complex **10a** (Scheme 6).

Figure 5 shows the ^{1}H NMR of the dearomatized dicarbonyl-Ru(II) complex **9a** (top) and the rearomatization of the pyridinic moiety and formation of the dicarbonyl-Ru(0) complex **10a** (bottom). It is worth noting the absence of the hydride around −4.3 ppm and the appearance of the methylenic arm as a multiplet at 2.7 ppm in the product, as well as the modification of the aromatic and aliphatic regions due to the aromatization process.

While attempts at dearomatization of the oxobispyridine complex **6c** led to mixtures, as described above, performing the deprotonation under CO afforded the corresponding dicarbonyl-dearomatized Ru(II) complex **9c** as a single product (Scheme 7). Interestingly, in contrast to complex **9a**, rearrangement to the corresponding Ru(0) complex was not

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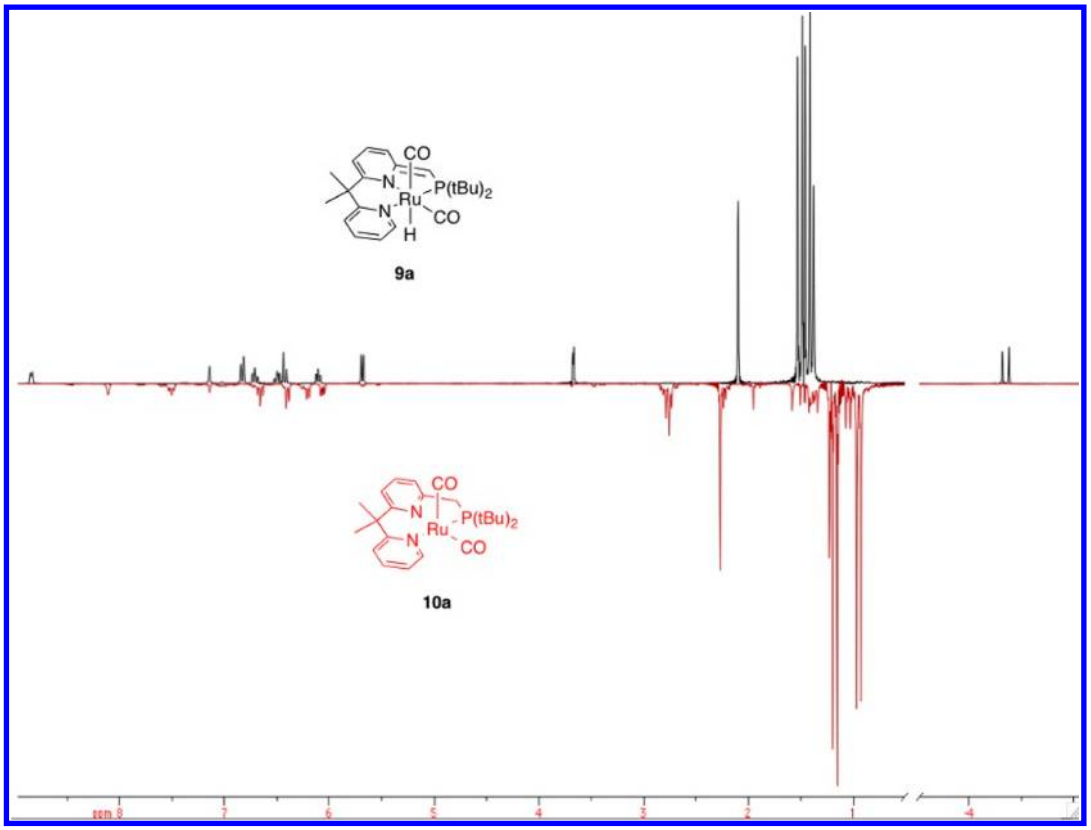
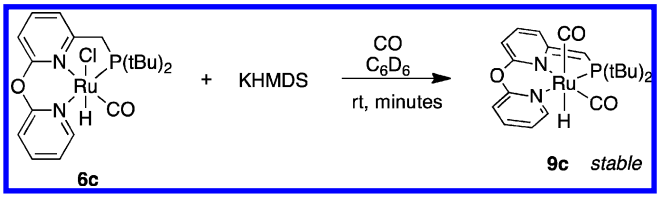


Figure 5. ^{1}H NMR of the dearomatized dicarbonyl-Ru(II) complex **9a** (top) and the rearomatization of the pyridinic moiety and formation of the dicarbonyl-Ru(0) complex **10a** (bottom).

Scheme 7



observed under these conditions. Formation of **9c** suggests that deprotonation of **6c** in the absence of CO does lead to the dearomatized complex, which is probably unstable and reacts further; coordination of an additional CO ligand to form a coordinatively saturated complex stabilizes it. The unobserved rearrangement of the Ru(II) complex **9c** to the corresponding Ru(0) complex may be due to the electron-donating bridging oxygen atom, which results in stabilization of the higher metal oxidation state.

Catalytic Activity. The catalytic activity of the new PNN-Ru complexes was tested in the hydrogenation of secondary amides. Better results were obtained with these complexes, and the results are presented in Table 2.

Hydrogenation of secondary amides afforded primary alcohols and primary amines in moderate yields. When 1 mol % of the dearomatized complex **7b** was utilized as catalyst for the reduction of *N*-phenylacetamide, the corresponding ethanol and aniline were obtained in 52% and 57% yields, respectively (entry 1, Table 2). When the cyclometalated complex **8b** was employed for the hydrogenation of *N*-phenylacetamide, lower yields of ethanol (22%) and aniline (25%) were obtained (entry 2, Table 2). It is clear that the cyclometalation is again detrimental for the catalysis. An additional experiment using the conditions described in entry 1 of Table 2, but extending the reaction time (72 h), resulted in an increased yield of 63% of ethanol and 65% of aniline (entry 3, Table 2).

This reaction was also tested with other amides such as *N*-benzyl-benzylamide and *N*-phenyl-benzylamide, obtaining moderate yields of the corresponding alcohols and amines (entries 4 and 5, Table 2). Hydrogenation of amides to alcohols and amines is a difficult transformation, and only very few examples for this reaction were reported.[4b,10]

The catalytic activity of the new PNN-Ru complexes was also tested in several reactions, including coupling of alcohols with amines and esterification of primary alcohols (see Supporting Information). The results are compared with the parent pyridine- and bipyridine-based catalysts and found that PNN-Ru complexes (**6a−c**, **7b**, **8a**, and **9c**) showed less activity toward catalysis.[2b,c,o] The low activity and selectivity of these bridged-bipyridine-based PNN-Ru(II) complexes in this reaction is likely a result of the cyclometalation of the active species **7a** and **7b**, which is detrimental to the catalysis. The low stability of the expected dearomatized complex formed by deprotonation of **6c** was also detrimental to catalysis. Hence, these PNN complexes are much less active than the previously reported amine-pyridine-based PNN and PNP-Ru(II) complexes, which presented high activity and selectivity toward amidation[2c] and imine synthesis[2d] reactions, respectively.

Thus, it is clear that the low activity of the PNN-Ru complexes evaluated in this work is directly related to the cyclometalation of the dearomatized complexes. In previous reports,[1−5] it was shown that these transformations involve dearomatized, pyridine- and bipyridine- based catalysts, which are able to add alcohols, followed by hydride elimination and liberation of dihydrogen as key steps. With the cyclometalated

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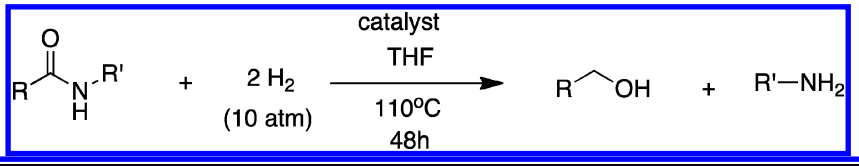
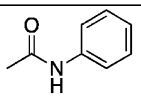
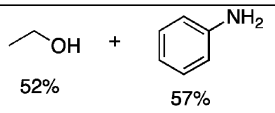
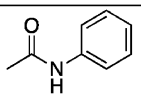
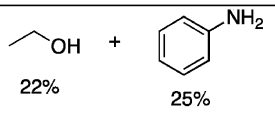
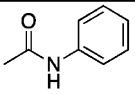
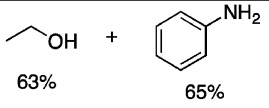
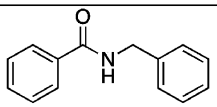
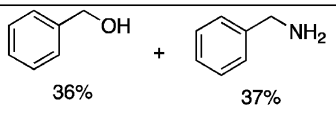
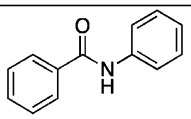
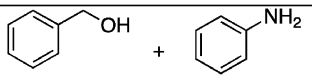
Table 2.



Entry[a]	Catalyst	Substrate	Conversion (%)[b]
1	**7b** (1 mol%)		 52% 57%
2	**8b** (1 mol%)		 22% 25%
3[c]	**7b** (1 mol%)		 63% 65%
4	**7b** (1 mol%)		 36% 37%
5	**7b** (1 mol%)		 51% 48%

[a]Reaction procedure: A Fischer–Porter tube was charged with 1 mmol of amide, 0.01 mmol of catalytic precursor, 10 atm of H_2, 1 mmol of mesitylene as internal standard in each experiment, and 2 mL of THF as solvent, and the solution was heated at 110 °C for 48 h. [b]Conversions were determined by CG and GC-MS. [c]Reaction time: 72 h.

compounds, these reactions are inhibited due to the rearomatization of the pyridine ring and the saturation of the ruthenium center. In addition, the hydride ligand of complexes **8a** and **8b** is located *trans* to the terminal pyridine ligand, rendering the hydride less hydridic and thus hampering the liberation of the required dihydrogen (by hydride coupling with a proton from the "arm"), and as a consequence catalysis is retarded. The much better results for hydrogenation of amides may be a consequence of the reversibility of the cyclometalation process under hydrogen pressure.

■ CONCLUSION

New pincer-ligand systems and complexes are described here. The reported diastereoselective cyclometalation reactions of the dearomatized complexes lead to novel complexes and provide another example of facile bond activation by metal–ligand cooperation, based on the concept of aromatization–dearomatization of the ligand. However, the intramolecular C–H activation process hinders intermolecular bond activation and has a negative impact on catalytic dehydrogenation reactions, but less so on catalytic hydrogenation; thus the rare hydrogenation of amides proceeds fairly well, probably as a result of reversal of the cyclometalation process.

■ EXPERIMENTAL SECTION

a. General Experimental Procedures. Unless otherwise noted, all experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with an MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were used as received. All solvents were degassed with argon and kept in the glovebox over 4 Å molecular sieves. Most of the chemicals used in catalysis reactions were purified according to standard procedures (or by vacuum distillation/sublimation). $RuHCl(PPh_3)_3(CO)$[11] was prepared according to literature procedures.

Thin-layer chromatography (TLC) was performed on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254, and the spots were visualized with UV light at 254 nm or under iodine. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60 (0.063–0.200 mm). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 300, 75, and 122 MHz, respectively, using Bruker AMX-300 and AMX-500 NMR spectrometers. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. $^{31}P\{^1H\}$ NMR chemical shifts are reported in parts per million downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets. Mass spectra were recorded on a Micromass Platform LCZ 4000, using electrospray ionization (ESI) mode. GC was performed using a Carboxen 1000 column on a HP 690 series GC system.

b. Synthesis of 2-Methyl-6-(pyridin-2-ylmethyl)pyridine (3). A dried three-neck round-bottom flask equipped with a stirring bar and connected to a vacuum-argon line, equipped with two rubber septa, was charged with 5 g (46.6 mmol, 1.0 equiv) of 2,6-lutidine and 10 mL of anhydrous THF. The flask was placed into a dry ice/acetone bath at −75 °C. Then 34.2 mL of a solution of *n*-BuLi (1.5 M in

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hexanes, 51.3 mmol, 1.1 equiv) was added dropwise at this temperature during 20 min. After this time 5.43 g (56 mmol, 1.2 equiv) of 2-fluoropyridine was added dropwise during 20 min at −75 °C and stirred for an additional hour. The solution was allowed to warm at room temperature and stirred for 5 h at this temperature. A 5 mL amount of an aqueous solution of NH_4Cl was added at 0 °C to quench the reaction, and the solvent was removed under vacuum. Then 10 mL of ethyl acetate was added, and the organic phase was washed three times with 10 mL of an aqueous solution of $NaHCO_3$. The solvent was removed under vacuum, and the compound was purified on a column of neutral alumina using a mixture of hexanes/ethyl acetate (9.5:0.5) as eluent. Product **3** was obtained as a yellow oil in 80% yield (6.9 g).

^{1}H NMR ($CDCl_3$): 8.49 (d, J = 5.0 Hz, 1H, Py), 7.6 (t, J = 7.5 Hz, 1H, Py), 7.4 (t, J = 7.5 Hz, 1H, Py), 7.1 (d, J = 8.0 Hz, 1H, Py), 7.0 (m, 1H, Py), 6.9 (m, 2H, Py), 4.4 (s, 2H, Py-$\underline{CH_2}$-Py), 2.5 (s, 3H, $\underline{CH_3}$-Py). MS (EI$^+$): 184 (M^+).

c. Synthesis of 2-Methyl-6-(2-(pyridin-2-yl)propan-2-yl)-pyridine (4a). A dried three-neck round-bottom flask equipped with a stirring bar and connected to a vacuum-argon line, equipped with two rubber septa, was charged with 3 g (16.2 mmol, 1.0 equiv) of 2-methyl-6-(pyridin-2-ylmethyl)pyridine (**3**) and 15 mL of anhydrous THF. The flask was placed into a dry ice/acetone bath at −75 °C. Then 11.88 mL of a solution of *n*-Bu-Li (1.5 M in hexanes, 17.8 mmol, 1.1 equiv) was added dropwise at this temperature during 20 min. After this time 1.14 mL (2.52 mg, 17.8 mmol, 1.1 equiv) of methyl iodide was added dropwise during 15 min at −75 °C, and the solution was stirred for an additional hour. Then 11.9 mL of additional *n*-BuLi was added slowly, and the solution was stirred for a period of 1 h. Then 3.0 mL (6.9 mg, 48.6 mmol, 3 equiv) of methyl iodide was added with a syringe during 30 min, and the reaction was stirred for 2 h at −75 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h at this temperature. A 5 mL sample of an aqueous solution of NH_4Cl was added at 0 °C to quench the reaction, followed by removal of the solvent under vacuum. A 10 mL portion of ethyl acetate was added, and the organic phase was washed three times with 10 mL of aqueous $NaHCO_3$. The solvent was removed under vacuum, and the compound was purified on a column of neutral alumina using a mixture of hexanes/ethyl acetate (9.5:0.5) as eluent. The product **5a** was obtained as a colorless solid in 86% yield (2.9 g).

^{1}H NMR ($CDCl_3$): 8.5 (d, J = 5.0 Hz, 1H, Py), 7.5 (t, J = 7.5 Hz, 1H, Py), 7.4 (t, J = 7.5 Hz, 1H, Py), 7.2 (d, J = 8.0 Hz, 1H, Py), 7.1 (m, 1H, Py), 6.9 (m, 2H, Py), 2.5 (s, 3H, $\underline{CH_3}$-Py), 1.8 (s, 6H, Me_2C). MS (EI$^+$): 212 (M^+).

d. Synthesis of the Pincer-Type PNN Ligand 2a. A dried three-neck round-bottom flask equipped with a stirring bar and connected to a vacuum-argon line, equipped with two rubber septa, was charged with 1.18 g (5.5 mmol, 1.0 equiv) of 2-methyl-6-(2-(pyridin-2-yl)propan-2-yl)pyridine (**4a**) and 15 mL of anhydrous diethyl ether. The flask was placed into a dry ice/acetone bath at −75 °C under a constant flow of argon. Then 4.45 mL of a solution of *n*-BuLi (1.5 M in hexanes, 6.6 mmol, 1.1 equiv) was added dropwise at this temperature during 20 min. After this time a solution of 1.2 g (6.67 mmol, 1.1 equiv) of chlorodi-*tert*-butylphosphine in 3 mL of ether was transferred via cannula into the flask and stirred at this temperature for a period of 3 h. The reaction mixture was allowed to warm to room temperature and stirred overnight under argon. The reaction mixture was quenched with 3 mL of deionized and deoxygenated water, the organic phase was transferred via cannula into a dried Schlenk flask connected to the vacuum-argon line, and the solvent was removed under vacuum. The resulting oil was transferred to a glovebox and dissolved in 10 mL of pentane, and the solution was dried over anhydrous Na_2SO_4. The pentane solution was passed through a column of neutral alumina, and the pentane was removed under vacuum. The product **2a** was obtained as a yellow oil in 93% yield (1.8 g).

^{1}H NMR (C_6D_6): 8.5 (d, J = 4.5 Hz, 1H, Py), 7.1 (m, 4H, Py), 6.8 (d, J = 7.2 Hz, 1H, Py), 6.6 (m, 1H, Py), 3.1 (d, J_{P-H} = 2.4 Hz, 2H, Py-$\underline{CH_2}$-P), 2.0 (s, 6H, Me_2C), 1.0 (d, J_{P-H} = 10.8 Hz, 18H, $\underline{t\text{-}Bu_2}$P). ^{31}P{^{1}H} NMR ($C_6D_6$): 39.5 (s). ^{13}C{^{1}H} NMR (C_6D_6): 168.1 (s, Py), 166.1 (s, Py), 161.0 (d, J_{P-C} = 13.8 Hz, Py), 148.4 (s, Py), 135.7 (s, Py), 135.2 (s, Py), 121.6, (s, Py), 121.2 (d, J_{P-C} = 8.8 Hz, Py), 120.6 (s, Py), 117.8 (s, Py), 32.3 (d, J_{P-C} = 26.4 Hz, Py-$\underline{CH_2}$-P), 31.7 (d, J_{P-C} = 23.8 Hz, P-$\underline{CMe_3}$), 29.7 (d, J_{P-C} = 13.8 Hz, $\underline{CMe_3}$), 28.7 (s, $\underline{Me_2C}$).

e. Synthesis of Complex 6a. A Schlenk vessel equipped with a stopcock, Rotaflo cap, and a stirring bar was charged with 817 mg (0.85 mmol, 1 equiv) of $RuHCl(CO)(PPh_3)_3$ and 300 mg of the PNN ligand **2a** (0.87 mmol, 1.02 equiv), which were then dissolved in 5 mL of THF. The reaction was set up into a thermostated oil bath at 65 °C for a period of 6 h. After this time, the solution was transferred to a vial and the solvent was concentrated under vacuum to 1 mL, and then 5 mL of pentane was added to precipitate the product. The solid was filtered off, washed with 5 mL of pentane (three times), and dried under vacuum for 4 h. The product **6a** was obtained as a light yellow solid in 89% yield (0.39 g).

^{1}H NMR (CD_2Cl_2): 9.5 (d, J = 5.4 Hz, 1H, Py), 7.77 (m, 3H, Py), 7.6 (d, J = 8.4 Hz, 1H, Py), 7.4 (d, J = 7.8 Hz, 1H, Py), 7.2 (t, J = 6.6 Hz, 1H, Py), 4.1 (dd, J_{P-H} = 7.8 Hz, J_{gem} = 16.5 Hz, 1H, Py-$\underline{CH_2}$-P), 3.6 (dd, J_{P-H} = 12.0 Hz, J_{gem}= 16.8 Hz, 1H, Py-$\underline{CH_2}$-P), 2.3 (s, 3H, Me_2C), 2.0 (s, 3H, Me_2C), 1.5 (d, J_{P-H} = 13.2 Hz, 9H, $\underline{t\text{-}Bu_2}$P), 1.2 (d, J_{P-H} = 12.6 Hz, 9H, $\underline{t\text{-}Bu_2}$P), −14.5 (d, J_{P-H} = 26.1 Hz, 1H, Ru-H). ^{31}P NMR (CD_2Cl_2): 108.5 (s). ^{13}C NMR (CD_2Cl_2): 207.1 (d, J_{P-C} = 17.7 Hz, CO), 163.6 (d, J_{P-C} = 5.3 Hz, Py), 163.2 (s, Py), 163.1 (s, Py), 158.3 (d, J_{P-C} = 2.03 Hz, Py), 137.7 (s, Py), 137.3 (s, Py), 122.3 (s, Py), 121.8 (d, J_{P-C} = 9.2 Hz, Py), 121.6 (d, J_{P-C} = 2.9 Hz, Py), 119.3 (s, Py), 47.1 (s, Py-$\underline{C}$-Py), 36.3 (d, J_{P-C} = 16.1 Hz, Py-$\underline{CH_2}$-P), 36.4 (d, J_{P-C} = 22.4 Hz, P-$\underline{CMe_3}$), 36.0 (d, J_{P-C} = 22.6 Hz, P-$\underline{CMe_3}$), 30.2 (d, J_{P-C} = 3.21 Hz, $\underline{CMe_3}$), 29.7 (s, $\underline{Me_2C}$), 28.3 (d, J_{P-C} = 3.5 Hz, $\underline{CMe_3}$), 26.1 (s, $\underline{Me_2C}$). MS (ESI, MeOH): 488 (100%, (M − Cl)$^+$).

f. Synthesis of Complex 7a by Dearomatization of 6a. An 18 mg (0.036 mmol, 1.0 equiv) portion of the PNN-Ru complex **6a** was suspended in 0.5 mL of toluene-d_8 into a vial, and the suspension was cooled at −35 °C for 15 min. Then 7 mg (0.036 mmol, 1.0 equiv) of potassium hexamethyldisilazane (KHMDS) was dissolved in 0.5 mL of toluene-d_8 and cooled at −35 °C for 15 min. The base was added slowly to the suspension of complex **6a**, resulting in an inmediate formation of a dark green solution. The solution was inmediatelly transferred into an NMR tube, and the NMR spectra of the dearomatized complex **7a** were inmediatly recorded at −35 °C.

^{1}H NMR (tol-d_8): 8.6 (d, J = 4.8 Hz, 1H, Py), 6.8 (t, J = 7.5 Hz, 1H, Py), 6.7 (d, J = 7.8 Hz, 1H, Py), 6.2 (m, 3H, Py), 5.3 (d, J = 6.3 Hz, 1H, Py), 3.5 (d, J_{P-H} = 1.8 Hz, 1H, P-CH═), 1.45 (d, J_{P-H} = 8.1 Hz, 9H, $\underline{t\text{-}Bu_2}$P), 1.39 (d, J_{P-H} = 7.5 Hz, 9H, $\underline{t\text{-}Bu_2}$P), 1.2 (s, 3H, Me_2C), 0.3 (s, 3H, Me_2C), −22.1 (d, J_{P-H} = 29.1 Hz, 1H, Ru-H). ^{31}P NMR (tol-d_8): 102.3 (s).

g. Formation of Complex 8a by Cyclometalation. A 24 mg (0.0459 mmol, 1 equiv) amount of the PNN-Ru complex **6a** was suspended in 2 mL of THF in a vial and cooled at −35 °C for 15 min. Then 5.6 mg (0.0505 mmol, 1.1 equiv) of *t*-BuOK was dissolved in 1 mL of THF and cooled at −35 °C for 15 min. The base was added dropwise into the suspension at −35 °C and stirred for a period of 30 min at this temperature, resulting in a dark green solution. The dark combined solution was stirred at room temperature during 4 h until the appearance of a yellow suspension of compound **8a**. The solution was concentrated under vacuum to a volume of 1 mL, and 5 mL of pentane was added to precipitate the product. The solid was washed with 5 mL of pentane (three times) and dried under vacuum for 4 h. The product was obtainded as a yellow solid in 97% (21 mg) yield. It is poorly soluble and nonreactive in benzene, toluene, acetone, MeOH, and THF.

^{1}H NMR (C_6D_6): 8.9 (d, J = 5.4 Hz, 1H, Py), 6.9 (t, J = 7.5 Hz, 2H, Py), 6.8 (t, J = 7.8 Hz, 1H, Py), 6.6 (d, J = 7.8 Hz, 1H, Py), 6.3 (d, J = 7.8 Hz, 1H, Py), 6.2 (t, J = 6.0 Hz, 1H, Py), 3.1 (dd, J_{P-H} = 6.0 Hz, J_{gem} = 16.2 Hz, 1H, Py-$\underline{CH_2}$-P), 2.9 (m, 2H, C-$\underline{CH_2}$-Ru), 2.4 (dd, J_{P-H} = 5.7 Hz, J_{gem}= 10.2 Hz, 1H, Py-$\underline{CH_2}$-P), 1.7 (s, 3H, $\underline{Me}$C), 1.5 (d, J_{P-H} = 12.0 Hz, 9H, $\underline{t\text{-}Bu_2}$P), 0.9 (d, J_{P-H} = 11.4 Hz, 9H, $\underline{t\text{-}Bu_2}$P), −12.1 (d, J_{P-H} = 20.4 Hz, 1H, Ru-H). ^{31}P NMR (C_6D_6): 108.2 (s). ^{13}C NMR (C_6D_6): the very low solubility of this complex in most of the solvents

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did not allow the observation of the quaternary carbons even at longer periods of adquisition; 155.0 (s, Py), 134.7 (s, Py), 134.4 (s, Py), 119.8 (s, Py), 119.5 (s, Py), 117.2 (d, J_{P-C} = 7.83 Hz, Py), 116.6 (s, Py), 48.9 (d, J_{P-C} = 62.4 Hz, Ru-CH_2-C), 37.3 (d, J_{P-C} = 13.4 Hz, Py-CH_2-P), 31.1 (d, J_{P-C} = 5.4 Hz, CMe_3), 29.1 (d, J_{P-C} = 7.9 Hz, CMe_3), 26.4 (d, J_{P-C} = 7.5 Hz, MeC). MS (ESI, MeOH): 486 (100%, $(M)^+$).

h. Synthesis of 2-Methyl-6-(1-(pyridin-2-yl)cyclopentyl)-pyridine (4b). A dried three-neck round-bottom flask equipped with a stirring bar and connected to a vacuum-argon line, equipped with two rubber septa, was charged with 1 g (5.4 mmol, 1.0 equiv) of 2-methyl-6-(pyridin-2-ylmethyl)pyridine (**3**) and 10 mL of anhydrous freshly distilled THF. The flask was placed in a dry ice/acetone bath at −75 °C, and 3.96 mL of a solution of *n*-BuLi (1.5 M in hexanes, 5.94 mmol, 1.1 equiv) was added dropwise at this temperature during 20 min. After this time, 0.752 mL (1.76 g, 5.7 mmol, 1.05 equiv) of 1,4-diiodobutane was added dropwise during 15 min at −75 °C and stirred for an additional hour. After this time, an additional 3.96 mL of *n*-BuLi was added slowly and stirred for 1 h at −75 °C. The solution was allowed to warm to room temperature and stirred for 3 h at this temperature. Then 5 mL of an aqueous solution of NH_4Cl was added at 0 °C to quench the reaction, and the solvent was removed under vacuum. A 10 mL sample of ethyl acetate was added to the mixture, and the organic phase was washed with 3 × 10 mL of aqueous $NaHCO_3$. The solvent was removed under vacuum, and the residue was purified using a column of neutral alumina using hexanes/ethyl acetate (9.5:0.5) as eluent. The product **4b** was obtained as a colorless solid in 75% yield (1.0 g).

^{1}H NMR ($CDCl_3$): 8.5 (d, *J* = 4.2 Hz, 1H, Py), 7.5 (t, *J* = 7.5 Hz, 1H, Py), 7.4 (t, *J* = 7.5 Hz, 1H, Py), 7.2 (d, *J* = 8.1 Hz, 1H, Py), 7.0 (m, 1H, Py), 6.9 (d, *J* = 7.8 Hz, 1H, Py), 6.8 (d, *J* = 7.5 Hz, 1H, Py), 2.6 (m, 4H, −CH_2−), 2.5 (s, 3H, Me-Py), 1.7 (m, 4H, −CH_2−). MS (EI^+): 238 (M^+).

I. Synthesis of Ligand 2b. A dried three-neck round-bottom flask equipped with a stirring bar and connected to a vacuum-argon line, equipped with two rubber septa, was charged with 0.262 g (1.1 mmol, 1.0 equiv) of 2-methyl-6-(1-(pyridin-2-yl)cyclopentyl)pyridine (**4b**) and 10 mL of anhydrous and freshly distilled diethyl ether. The flask was placed in a dry ice/acetone bath at −75 °C under a constant flow of argon. Then 0.88 mL of a solution of *n*-BuLi (1.5 M in hexanes, 1.32 mmol, 1.1 equiv) was added dropwise at this temperature during 20 min. A solution of $ClP(t\text{-}Bu)_2$ (0.238 mg, 1.32 mmol, 1.2 equiv) in 3 mL of ether was transferred via cannula into the flask and stirred at −75 °C for a period of 3 h. The reaction was allowed to warm to room temperature and stirred overnight under argon flow. The reaction was quenched with 3 mL of deionized and deoxygenated water, the organic phase was transferred via cannula into a dried Schlenk tube connected to a vacuum-argon line, and the solvent was removed under vacuum. The resulting oil was dissolved in 10 mL of pentane in a glovebox and dried with anhydrous Na_2SO_4. The pentane solution was passed through a column of neutral alumina, and the pentane was removed under vacuum during 4 h. The product **2b** was obtained as yellow oil in 94% (0.395 g) yield.

^{1}H NMR (C_6D_6): 8.4 (d, *J* = 4.2 Hz, 1H, Py), 7.1 (t, *J* = 7.8 Hz, 1H, Py), 7.09 (t, *J* = 5.4 Hz, 1H, Py), 6.9 (m, 3H, Py), 6.5 (m, 1H, Py), 3.0 (d, J_{P-H} = 2.4 Hz, 2H, Py-CH_2-P), 2.8 (m, 4H, −CH_2−), 1.8 (m, 4H, −CH_2−), 1.1 (d, J_{P-H} = 10.5 Hz, 18H, *t*-Bu_2P). ^{31}P NMR (C_6D_6): 39.5 (s). ^{13}C{^{1}H} NMR (C_6D_6): 168.0 (s, Py), 166.2 (s, Py), 161.1 (d, J_{P-C} = 12.9 Hz, Py), 148.4 (s, Py), 135.1 (s, Py), 134.7 (s, Py), 121.6 (s, Py), 121.4 (d, J_{P-C} = 7.6 Hz, Py), 119.9 (s, Py), 117.6 (s, Py), 32.5 (d, J_{P-C} = 26.8 Hz, Py-CH_2-P), 31.6 (d, J_{P-C} = 23.5 Hz, P-CMe_3), 29.5 (d, J_{P-C} = 13.4 Hz, CMe_3), 22.4 (s, −CH_2−), 22.1 (s, −CH_2−).

j. Synthesis of Complex 6b. A Schlenk vessel equipped with a stopcock, a Rotaflo cap, and a stirring bar was charged with 300 mg (0.31 mmol, 1 equiv) of $RuHCl(CO)(PPh_3)_3$ and 131 mg of the PNN ligand **2b** (0.34 mmol, 1.1 equiv) dissolved in 5 mL of THF. The reaction was set up in an oil bath at 65 °C for a period of 6 h. After this time, the solution was transferred into a vial, the solvent was removed up to 1 mL, and then 5 mL of pentane was added, allowing the precipitation of the product. The solid was filtered and washed with 5 mL of pentane (three times) and dried under vacuum for 4 h. The product **6b** was obtained as a light yellow solid in 94% yield (0.135 g).

^{1}H NMR (CD_2Cl_2): 9.4 (d, *J* = 5.1 Hz, 1H, Py), 7.7 (m, 2H, Py), 7.5 (d, *J* = 8.1 Hz, 1H, Py), 7.4 (d, *J* = 8.1 Hz, 1H, Py), 7.2 (m, 1H, Py), 7.1 (m, 1H, Py), 4.1 (dd, J_{P-H} = 7.8 Hz, J_{gem} = 16.8 Hz, 1H, Py-CH_2-P), 3.6 (dd, J_{P-H} = 11.7 Hz, J_{gem} = 17.1 Hz, 1H, Py-CH_2-P), 3.5 (m, 1H, −CH_2−), 3.0 (m, 1H, −CH_2−), 2.6 (m, 3H, −CH_2−), 1.9 (m, 3H, −CH_2−), 1.5 (d, J_{P-H} = 13.5 Hz, 9H, *t*-Bu_2P), 1.2 (d, J_{P-H} = 12.9 Hz, 9H, *t*-Bu_2P), −14.5 (d, J_{P-H} = 26.1 Hz, 1H, Ru-H). ^{31}P NMR (CD_2Cl_2): 108.9 (s). ^{13}C NMR (CD_2Cl_2): 207.2 (d, J_{P-C} = 17.4 Hz, CO), 163.5 (d, J_{P-C} = 4.8 Hz, Py), 158.3 (d, J_{P-H} = 1.8 Hz, Py), 137.4 (d, J_{P-C} = 1.2 Hz, Py), 137.1 (s, Py), 134.4 (t, J_{P-C} = 5.6 Hz, Py), 127.4 (d, J_{P-C} = 4.7 Hz, Py), 122.2 (d, J_{P-C} = 1.2 Hz, Py), 122.0 (d, J_{P-C} = 2.6 Hz, Py), 121.6 (d, J_{P-C} = 9.6 Hz, Py), 119.8 (s, Py), 59.6 (bd, CH_2-P), 36.5 (s, −CH_2−), 36.1 (m, −CH_2−, CMe_3), 30.2 (d, J_{P-C} = 3.2 Hz, CMe_3), 29.3 (d, J_{P-C} = 3.2 Hz, CMe_3), 22.5 (s, −CH_2−), 22.1 (s, −CH_2−). MS (ESI, MeOH): 514 (100%, $(M - Cl)^+$).

k. Synthesis of the Dearomatized Complex 7b. A 27 mg (0.049 mmol, 1 equiv) amount of the PNN-Ru complex **6b** was suspended in 2 mL of THF in a vial and cooled at −35 °C for 15 min. A solution of *t*-BuOK (5.6 mg, 0.0501 mmol, 1.1 equiv) in 1 mL of THF was cooled at −35 °C for 15 min and then added dropwise to the suspension of **6b** at −35 °C during 30 min, and the solution was stirred at this temperature for 2 h. The solution was filtered over Celite, and the Celite was washed with 2 mL of cold THF. The combined solvent was removed under vacuum, and the sample was dried under vacuum for a period of 4 h. The product **7b** was obtainded as a dark green solid in 94% yield (23 mg).

^{1}H NMR (C_6D_6): 8.5 (d, *J* = 5.08 Hz, 1H, Py), 6.9 (m, 1H, Py), 6.8 (t, *J* = 7.7 Hz, 1H, Py), 6.7 (d, *J* = 7.79 Hz, 1H, Py), 6.3 (m, 1H, Py), 6.2 (m, 2H, Py), 5.3 (d, *J* = 6.3 Hz, 1H, Py), 3.5 (d, J_{P-H} = 2.24 Hz, 1H, =CH-P), 2.0 (m, 1H, −CH_2−), 1.6 (m, 3H, −CH_2−), 1.4 (d, J_{P-H} = 9.8 Hz, 9H, *t*-Bu_2P), 1.39 (d, J_{P-H} = 9.7 Hz, 9H, *t*-Bu_2P), 1.2 (m, 2H, −CH_2−), 0.8 (m, 1H, −CH_2−), 0.2 (m, 1H, −CH_2−), −21.9 (d, J_{P-H} = 29.2 Hz, 1H, Ru-H). ^{31}P NMR (C_6D_6): 102.7 (s). ^{13}C NMR (C_6D_6): 214.7 (d, J_{P-C} = 13.3 Hz, CO), 167.0 (d, J_{P-C} = 7.01 Hz, Py), 166.4 (d, J_{P-C} = 1.28 Hz, Py), 162.7 (d, J_{P-C} = 8.67 Hz, Py), 154.5 (s, Py), 135.2 (s, Py), 134.2 (s, Py) 119.7 (d, J_{P-C} = 11.04 Hz, Py), 118.3 (s, Py) 117.2 (d, J_{P-C} = 7.5 Hz, Py), 76.6 (d, J_{P-C} = 2.4 Hz, Py), 67.2 (d, J_{P-C} = 65.9 Hz, =CH-P), 37.5 (d, J_{P-C} = 13.06 Hz, −CH_2−), 36.5 (s, spiro-C), 36.4 (s, −CH_2−), 34.2 (d, J_{P-C} = 10.7 Hz, −CH_2−), 31.6 (d, J_{P-C} = 6.12 Hz, CMe_3), 31.1 (d, J_{P-C} = 5.09 Hz, CMe_3), 29.0 (d, J_{P-C} = 8.2 Hz, CMe_3), 26.2 (d, J_{P-C} = 7.12 Hz, CMe_3). MS (ESI, MeCN): 513 (100%, $(M + 1)^+$).

l. Synthesis of Complex 8b. A 23 mg (0.044 mmol) portion of the dearomatized compound **7b** was dissolved in 0.7 mL of benzene-d_6 and introduced into an NMR tube. The reaction was monitored via ^{1}H and ^{31}P NMR until disappearance of the starting material after 5 days.

^{1}H NMR (C_6D_6): 8.8 (d, *J* = 5.21 Hz, 1H, Py), 6.9 (d, *J* = 7.6 Hz, 1H, Py), 6.8 (t, *J* = 7.5 Hz, 1H, Py), 6.7 (d, *J* = 7.5 Hz, 1H, Py), 6.7 (d, *J* = 7.6 Hz, 1H, Py), 6.3 (d, *J* = 7.3 Hz, 1H, Py), 6.2 (t, *J* = 6.4 Hz, 1H, Py), 3.0 (dd, J_{P-H} = 6.0 Hz, J_{gem} = 16.2 Hz, 1H, Py-CH_2-P), 2.8 (dd, J_{P-H} = 8.0 Hz, J_{gem} = 15.9 Hz, 1H, Py-CH_2-P), 2.6 (m, 1H, −CH_2−), 2.4 (m, 1H, −CH_2−), 1.9 (m, 1H, CH_2-CH-Ru), 1.7 (m, 4H, −CH_2−), 1.4 (d, J_{P-H} = 11.8 Hz, 9H, *t*-Bu_2P), 0.8 (d, J_{P-H} = 11.3 Hz, 9H, *t*-Bu_2P), −12.5 (d, J_{P-H} = 19.9 Hz, 1H, Ru-H). ^{31}P NMR (C_6D_6): 109.4 (s). ^{13}C NMR (C_6D_6): 214.69 (d, J_{P-C} = 8.3 Hz, CO), 166.9 (d, J_{P-C} = 9.5 Hz, Py), 166.4 (s, Py), 162.8 (d, J_{P-C} = 8.7 Hz, Py), 154.5 (s, Py), 135.1 (s, Py), 134.2 (s, Py) 119.8 (s, Py), 119.7 (s, Py), 118.3 (s, Py), 117.2 (d, J_{P-C} = 7.6 Hz, Py), 76.6 (d, J_{P-C} = 2.8 Hz, Py-C-Py), 67.2 (d, J_{P-C} = 66.2 Hz, CH_2-CH-Ru), 37.3 (d, J_{P-C} = 13.05 Hz, =CH-P), 36.5 (d, J_{P-C} = 10.8 Hz, CMe_3), 36.4 (s, −CH_2−), 34.2 (d, J_{P-C} = 10.8 Hz, CMe_3), 31.6 (d, J_{P-C} = 6.09 Hz, −CH_2−), 31.1 (d, J_{P-C} = 5.2 Hz, CMe_3), 29.0 (d, J_{P-C} = 7.9 Hz, CMe_3), 26.2 (d, J_{P-C} = 7.4 Hz, −CH_2−). MS (ESI, MeOH): 513 (100%, $(M + 1)^+$).

m. Synthesis of 2-Methyl-6-(pyridin-2-yloxy)pyridine (5). A Schlenk vessel equipped with a stopcock, a Rotaflo cap, and a stirring bar was charged with 300 mg (1.91 mmol, 1 equiv) of 2-bromopyridine, 250 mg (2.29 mmol, 1.2 equiv) of 6-methyl-2-

hydroxypyridine, 530 mg (3.85 mmol, 2 equiv) of K_2CO_3, 33.2 mg (0.28 mmol, 0.15 equiv) of *N,N,N′,N′*-tetramethylethylenediamine, 18 mg (0.095 mmol, 0.05 equiv) of CuI, and 5 mL of anhydrous DMF. The solution was stirred and heated at 110 °C for a period of 48 h. After this time, 15 mL of ethyl acetate was added to the solution, and it was washed with 50 mL of a saturated aqueous solution of sodium chloride three times. The organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed under vacuum. The product was purified by chromatography on a column of neutral alumnia using a mixture of hexane/ethyl acetate (90:10) as eluent. Product **5** was obtained as a yellow oil in 81% (287 mg) yield.

^{1}H NMR ($CDCl_3$): 8.24 (d, J = 4.2 Hz, 1H, Py), 7.7 (t, J = 7.38 Hz, 1H, Py), 7.6 (t, J = 7.71 Hz, 1H, Py), 7.1 (m, 2H, Py), 6.9 (d, J = 7.47 Hz, 1H, Py), 6.8 (d, J = 8.2 Hz, 1H, Py), 2.5 (s, 3H, CH_3-Py). ^{13}C NMR ($CDCl_3$): 162.3 (s, Py), 160.7 (s, Py), 157.82 (s, Py), 147.7 (s, Py), 139.6 (s, Py), 139.4 (s, Py), 119.7 (s, Py), 119.3 (s, Py), 113.2 (s, Py), 111.18 (s, Py), 24.1 (s, CH_3-Py). MS (EI$^+$): 186 (M^+).

n. Synthesis of Phosphine Ligand 2c. A dried three-neck round-bottom flask equipped with a stirring bar and connected to a vacuum-argon line, equipped with two rubber septa, was charged with 250 mg (1.3 mmol, 1.0 equiv) of 2-methyl-6-(pyridin-2-yloxy)pyridine (**5**) and 15 mL of anhydrous diethyl ether. The flask was placed in a dry ice/acetone bath at −75 °C under a constant flow of argon. The 1 mL of a solution of *n*-BuLi (1.5 M in hexanes, 1.4 mmol, 1.1 equiv) was added dropwise at this temperature during 20 min. After this time a solution of ClP(*t*-Bu)$_2$ (266 mg, 1.4 mmol, 1.1 equiv) in 3 mL of ether was transferid via cannula into the flask, and the resulting solution was stirred at −75 °C for 3 h. The reaction was allowed to warm to room temperature and stirred overnight under argon. After this time the reaction was quenched with 3 mL of deionized and deoxygenated water, the organic phase was transferred via cannula into a dried Schlenk tube connected to a vacuum-argon line, and the solvent was removed under vacuum. The resulting oil was dissolved in 10 mL of pentane in a glovebox and dried with anhydrous Na_2SO_4. The pentane solution was passed through a column of neutral alumina, and the pentane was removed under vacuum during 4 h. The product **2c** was obtained as yellow oil in 76% (338 mg) yield.

^{1}H NMR (C_6D_6): 8.6 (d, J = 4.4 Hz, 1H, Py), 7.1 (t, J = 7.2 Hz, 1H, Py), 7.0 (t, J = 7.7 Hz, 1H, Py), 6.8 (d, J = 8.3 Hz, 1H, Py), 6.7 (m, 2H, Py), 6.5 (t, J = 6.5 Hz, 1H, Py), 2.8 (d, J_{P-H} = 2.9 Hz, 2H, Py-CH_2-P), 1.0 (d, J_{P-H} = 10.9 Hz, 18H, *t*-Bu$_2$P). ^{31}P NMR (C_6D_6): 39.2 (s). ^{13}C NMR (C_6D_6): 161.5 (s, Py), 161.4 (s, Py), 161.3 (s, Py), 147.8 (s, Py), 138.8 (s, Py), 138.4 (s, Py), 119.7 (d, J_{P-C} = 9.46 Hz, Py), 118.9 (s, Py), 113.7 (s, Py), 110.5 (d, J_{P-C} = 8.8 Hz, Py), 31.6 (d, J_{P-C} = 3.9 Hz, P-CMe_3), 31.3 (d, J_{P-C} = 5.9 Hz, P-CMe_3), 29.4 (d, J_{P-C} = 13.8 Hz, CMe_3), 27.5 (d, J_{P-C} = 17.0 Hz, P-CH_2-Py).

o. Synthesis of Complex 6c. A Schlenk vessel equipped with a stopcock, a Rotaflo cap, and a stirring bar was charged with 524 mg (0.55 mmol, 1 equiv) of RuHCl(CO)(PPh_3)$_3$ and a solution of 200 mg of the PNN ligand **2c** (0.6 mmol, 1.1 equiv) in 5 mL of THF. The solution was heated in an oil bath at 65 °C for a period of 6 h. After this time, the solution was transferred into a vial, the solvent was concentrated to 1 mL, and then 5 mL of pentane was added, allowing the precipitation of the product. The solid was filtered off, washed with 3 × 5 mL of pentane, and dried under vacuum for 4 h. The product **6c** was obtained as a light yellow solid in 91% yield (0.275 g).

^{1}H NMR (CD_2Cl_2): 8.9 (d, J = 5.8 Hz, 1H, Py), 7.8 (m, 2H, Py), 7.4 (d, J = 7.4 Hz, 1H, Py), 7.3 (d, J = 8.3 Hz, 1H, Py), 7.2 (t, J = 6.6 Hz, 1H, Py), 7.12 (d, J = 8.1 Hz, 1H, Py), 3.8 (dd, J_{P-H} = 8.87 Hz, J_{gem}= 16.21 Hz, 1H, Py-CH_2-P), 3.4 (dd, J_{P-H} = 10.43 Hz, J_{gem} = 16.1 Hz, 1H, Py-CH_2-P), 1.5 (d, J_{P-H} = 13.24 Hz, 9H, *t*-Bu$_2$P), 1.2 (d, J_{P-H} = 12.9 4 Hz, 9H, *t*-Bu$_2$P), −14.48 (d, J_{P-H} = 23.56 Hz, 1H, Ru-H). ^{31}P NMR (CD_2Cl_2): 112.8 (s). ^{13}C NMR (CD_2Cl_2): 206.4 (d, J_{P-C} = 17.19 Hz, CO), 162.0 (d, J_{P-C} = 4.6 Hz, Py), 158.5 (s, Py), 158.3 (s, Py), 154.5 (d, J_{P-C} = 1.68 Hz, Py), 140.66 (s, Py), 140.22 (s, Py), 121.1 (d, J_{P-C} = 1.10 Hz, Py), 119.5 (d, J_{P-C} = 8.6 Hz, Py), 115.6 (d, J_{P-C} = 1.62 Hz, Py), 112.4 (s, Py), 36.9 (d, J_{P-C} = 17.24 Hz, CMe_3) 35.8 (d, J_{P-C} = 23.12 Hz, CMe_3), 35.7 (d, J_{P-C} = 16.87 Hz, P-CH_2-Py), 29.7 (d, J_{P-C} = 3.6 Hz, CMe_3), 28.9 (d, J_{P-C} = 3.2 Hz, CMe_3). MS (ESI, MeOH): 562 (100%, (M − Cl)$^+$).

p. Dearomatization in the Presence of CO. Synthesis of Complexes 9a and 10a. A 20 mL vial equipped with a cap with a septum was charged with 25 mg (0.047 mmol, 1 equiv) of complex **6a** and 1 mL of C_6D_6. The suspension in the vial was stirred and bubbled with CO, and then a solution of KHMDS (10 mg, 0.05 mmol, 1.05 equiv) in 0.5 mL of C_6D_6 was injected with a syringe into the reaction mixture at room temperature. A red solution of complex **9a** appeared immediately. The solution was introduced into an NMR tube and characterized. The conversion of **9a** into **10a** was followed at room temperature by ^{1}H and ^{31}P NMR for a period of 19 h until complex **9a** completely disappeared.

Complex **9a**: ^{1}H NMR (C_6D_6): 8.8 (d, J = 5.73 Hz, 1H, Py), 6.8 (d, J = 6.8 Hz, 1H, Py), 6.7 (t, J = 7.44 Hz, 1H, Py), 6.5 (t, J = 7.44 Hz, 1H, Py), 6.4 (d, J = 8.6 Hz, 1H, Py), 6.1 (t, J = 6.3 Hz, 1H, Py), 5.7 (d, J = 6.7 Hz, 1H, Py), 3.6 (d, J_{P-H} = 2.6 Hz, 1H, =CH-P), 2.1 (s, 3H, CH_3-C), 1.5 (d, J_{P-H} = 13.7 Hz, 9H, *t*-Bu$_2$P), 1.4 (d, J_{P-H} = 13.5 Hz, 9H, *t*-Bu$_2$P), 1.37 (s, 3H, CH_3-C), −4.34 (d, J_{P-H} = 18.8 Hz, 1H, Ru-H). ^{31}P NMR (C_6D_6): 99.32 (s).

Complex **10a**: ^{1}H NMR (C_6D_6): 8.1 (br s, 1H, Py), 7.5 (t, J = 7.2 Hz, 1H, Py), 6.6 (t, J = 7.7 Hz, 1H, Py), 6.4 (d, J = 7.8 Hz, 1H, Py), 6.2 (d, J = 7.7 Hz, 1H, Py), 6.0 (m, 2H, Py), 2.7 (m, 2H, Py-CH_2-P), 2.2 (s, 3H, CH_3-C), 1.3 (s, 3H, CH_3-C), 1.1 (d, J_{P-H} = 13.37 Hz, 9H, *t*-Bu$_2$P), 0.94 (d, J_{P-H} = 12.7 Hz, 9H, *t*-Bu$_2$P). ^{31}P NMR (C_6D_6): 100.8 (s).

q. Dearomatization in the Presence of CO. Synthesis of Complex 9c. A 20 mL vial equipped with a cap with a septum was charged with 25 mg (0.05 mmol, 1 equiv) of complex **6c** and 1 mL of C_6D_6. Then 10.5 mg (0.052 mmol, 1.05 equiv) of KHMDS was dissolved in 0.5 mL of C_6D_6 and charged in a syringe. The suspension in the vial was stirred and bubbled with CO, and then the KHMDS solution was injected into the reaction mixture at room temperature. An orange solution of complex **9c** appeared immediately. The solution was introduced into an NMR tube and characterized. The product was stable in solution for several days according to ^{1}H and ^{31}P NMR.

^{1}H NMR (C_6D_6): 8.17 (brd, J_{P-H} = 6.0 Hz, 1H, Py), 6.54 − 6.58 (m, 2H, Py), 6.42 (brd, J_{P-H} = 9.0 Hz, 1H, Py), 6.35 (d, J_{P-H} = 9.0 Hz, 1H, Py), 5.90 (d, J_{P-H} = 6.0 Hz, 1H, Py), 5.50 (d, J_{P-H} = 6.0 Hz, 1H, Py), 3.73 (d, J_{P-H} = 3.0 Hz, 1H, =CH-P), 1.48 (d, J_{P-H} = 15.0 Hz, 9H, *t*Bu$_2$P), 1.27 (d, J_{P-H} = 15.0 Hz, 9H, *t*Bu$_2$P), −4.41 (d, J_{P-H} = 24.0 Hz, 1H, Ru-H). ^{31}P NMR (C_6D_6): 99.32 (s). ^{13}C NMR (C_6D_6): 204.0 (d, J_{P-C} = 16.5 Hz, Ru-$CO_{(a)}$), 169.7 (d, J_{P-C} = 18.0 Hz, Ru-$CO_{(b)}$), 161.3 (s, Py-$C_{(quart)}$), 158.1 (s, Py-$C_{(quart)}$), 153.7 (s, Py-C), 140.1 (s, Py-C), 133.4 (s, Py-C), 120.1 (s, Py-C), 116.4 (s, Py-C), 112.1 (s, Py-C), 111.9 (s, Py-C), 88.3 (s, Py-C=CH-), 64.5 (d, J_{P-C} = 70.5 Hz, =CH-P), 38.2 (d, J_{P-C} = 22.5 Hz, $C_{(a)}(CH_3)_3$), 34.7 (brs, $C_{(b)}Me_3$), 31.2 (d, J_{P-C} = 4.5 Hz, C($C_{(a)}H_3$)$_3$), 29.0 (d, J_{P-C} = 6.0 Hz, C($C_{(b)}H_3$)$_3$).

r. Hydrogenation of Amides to Corresponding Alcohols and Amines. A 100 mL Fischer−Porter tube was charged under nitrogen with the ruthenium catalyst (0.01 mmol), an amide (1.0 mmol), and THF (2 mL). The nitrogen present in the Fischer−Porter (100 mL) was replaced by H_2 (three times with 30 psi) at room temperature; then it was filled with H_2 (10 atm). The solution was heated at 110 °C (bath temperature) with stirring for 48 h or longer. After cooling to room temperature, the H_2 was vented off carefully and the products were determined by GC with mesitylene as internal standard, using a Carboxen 1000 column on an HP 690 series GC system.

s. X-ray Crystal Structure Determination of Complexes 6a, 6b, and 8a. Crystals were placed in Paratone oil (Hampton Research), mounted in a MiTeGen loop, and flash frozen in a nitrogen stream at 100 K. Data were collected on a Bruker APEX-II Kappa CCD diffractometer mounted on a FR590 generator equipped with a sealed tube with Mo Kα radiation (λ = 0.71073 Å), MiraCol optics, and a graphite monochromator. The data were processed and scaled using the Bruker Apex2 SAINT suite. The structures were solved using direct methods with SHELXS-97 based on F^2. CIF files are included as separate files.

■ ASSOCIATED CONTENT

Supporting Information

Catalytic experiments, copies of NMR spectra of complexes **6a**, **6b**, **6c**, **7a**, **7b**, **8a**, **8b**, and **9c**, and CIF files giving X-ray data for **6a**, **6b**, and **8a** are included. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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