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New N,N,N-Donors Resulting in Highly Active Ruthenium Catalysts for Transfer Hydrogenation at Room Temperature

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A series of ruthenium complexes of the general formula $[RuCl_2(L)(NNN)]$ were synthesized starting from tridentate N,N,N-ligands containing pyridine and allylated pyrazole donor groups and $[RuCl_2(PPh_3)_3]$. The N,N,N-donors introduced herein are accessible in a few steps from versatile precursors. The primary products, $[RuCl_2(NNN)(PPh_3)]$, can be converted into the corresponding carbonyl complexes, $[RuCl_2(CO)(NNN)]$, by bubbling CO into a solution in toluene at elevated temperatures. All ruthenium complexes were investigated as catalysts for the transfer hydrogenation of aryl ketones. The phosphane complexes show high activities with turnover frequency values of up to 1200 h^{-1} in the presence of just one equivalent of KOH, whereas the carbonyl complexes are only poorly active.

Introduction

Aliphatic and aromatic nitrogen donors have emerged as important ligands in homo- and heterogeneous catalysis.[1,2] Among them, tridentate aromatic nitrogen donors have been used for nickel-catalyzed asymmetric Negishi cross-couplings[2e,2f] or for iron/cobalt-catalyzed ethylene polymerization.[3] Furthermore, polydentate imino and amino ligands have provided a considerable improvement on the catalyst performance in the catalytic transfer hydrogenation of ketones.[4]

In this transformation, the substrates are reduced to alcohols with 2-propanol or formic acid as the hydrogen source.[5] Highly active catalytic systems make this approach attractive for the preparation of alcohols because the direct hydrogenation process requires handling of dangerous dihydrogen, often under elevated pressure. The most active systems are based on ruthenium, rhodium, and iridium as the catalytically active metal site coordinated by nitrogen and/or phosphorus ligands. In particular, ruthenium complexes containing suitable combinations of P- and N- or mixed P,N-ligands turned out to be efficient catalysts for the hydrogenation and transfer hydrogenation of carbonyl compounds. Thus, bi-, tri-, and tetradentate achiral and chiral ligands have successfully been used for the preparation of these catalysts. A few general types should be mentioned here: $[RuCl_2(NN)(P)_2]$ and $[RuCl_2(NN)(PP)]$ (P = phosphane ligand; PP = diphosphane ligand; NN = diamine, dipyridine ligand),[6] $[RuCl_2(P)_2(PN)]$ (PN = amino- or iminophosphane ligands, oxazolinylferrocenylphosphane),[7] $[RuCl_2(PN)_2]$,[7a,8] $[RuCl(\eta^6\text{-}p\text{-cymene})(PN)][BF_4]$ (PN = phosphole–pyridine),[9] $[RuCl(\eta^6\text{-}p\text{-cymene})(NN)][BF_4]$,[10] $[RuCl_2(NPN)(P)]$,[11] $\{RuCl_2(NPN)\}$,[12] $[RuCl_2(NNN)(P)]$ (NPN and NNN = oxazoline-based ligands),[13] [RuCl-(CNN)(PP)] [PP = (*R*,*S*)-1-{2-[bis(4-methoxy-3,5-dimethylphenyl)phosphanyl]ferrocenyl}ethyldicyclohexylphosphane (Josiphos-type diphosphane) and CNN = amine/aryl/pyridine-based ligands][14] and $[RuCl_2(PNNP)]$ systems (PNNP = diphosphane/diamine ligands).[15]

Herein, we describe the synthesis and characterization of ruthenium complexes of the type $[RuCl_2(L)(NNN)]$ (L = PPh_3 or CO), with tridentate dipyrazolpyridines as N,N,N-ligands. These complexes efficiently catalyze the transfer hydrogenation of ketones in the presence of basic 2-propanol at room temperature with high turnover frequencies (TOFs) of up to 1200 h^{-1}.

Results and Discussion

Synthesis and Characterization of Ligands and Complexes

The tridentate N,N,N-ligands **2a**,**b** employed herein are accessible from versatile starting materials in good yields by regioselective allylation of 2,6-bis(1*H*-pyrazol-3-yl)pyridine (**1a**) or 2,6-bis(5-butyl-1*H*-pyrazol-3-yl)pyridine (**1b**; Scheme 1).[3h,16,17] We decided to introduce allylic side chains in the 1- and 1′-positions of the pyrazole rings to functionalize the ligand with substituents of moderate bulkiness. Furthermore, the allylic side chains should offer a chelating π-donating element, which is able to stabilize a 16 valence-electron (VE) ruthenium(II) intermediate in a hemilabile manner, but will not be hydrogenated itself under the given reaction conditions of transfer hydrogenation. De-

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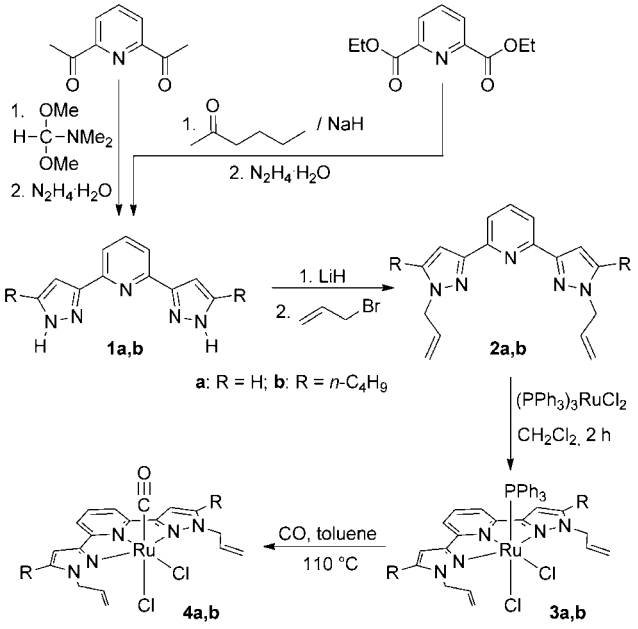
protonation of the pyrazole units with LiH in THF and subsequent allylation with allylic bromide gives **2a**,**b**. It should be noted here that the use of NaH for the deprotonation of **1a**,**b** leads to the formation of quite stable six-coordinate sodium complexes, which hamper the isolation of the target ligands.



Scheme 1. Allylation of dipyrazolylpyridines and subsequent formation of ruthenium(II) complexes.

By functionalizing the pyrazole ring with a butyl group (as in **2b**), the resonance of the proton in the 4-position of the pyrazole ring shifts about 0.75 ppm towards a higher field relative to **2a**, indicating an increased electron density in the pyrazole ring, which is also reflected in the ^{13}C NMR resonances of this compound. The methylene protons of the allylic side chains are doublets at δ = 4.83/4.62 ppm for compounds **2a/2b**, indicating that these hydrogen atoms are magnetically equivalent.

Treatment of **2a**,**b** with one equivalent of the ruthenium(II) precursor $[RuCl_2(PPh_3)_3]$ in dichloromethane at room temperature leads to the formation of the corresponding red-colored ruthenium(II) complexes **3a**,**b** in almost quantitative yields (Scheme 1). Typical for octahedral ruthenium(II) monophosphane complexes, the ^{31}P NMR resonances of **3a**,**b** are observed a δ = 44.20 and 42.71 ppm.[18] We recently published the reaction of the N,N,N-ligand **1b** (see Scheme 1), with N–H instead of *N*-allyl functions, with $[RuCl_2(PPh_3)_3]$.[19] This leads to a cationic ruthenium(II) complex of the type $[RuCl(\mathbf{1b})(PPh_3)_2]Cl$ with the two phosphane ligands *trans* to each other (^{31}P NMR: δ = 25.5 ppm). The ionic structure of this compound is stabilized by H···Cl interactions between the acidic N–H units at the two pyrazole rings and both the coordinated chloro ligand and the free chloride counteranion. In contrast to **3a**,**b** (see below), $[RuCl(\mathbf{1b})(PPh_3)_2]Cl$ shows just moderate transfer hydrogenation activities, which we assign to the cationic nature of the active site and to steric hindrance between the two triphenylphosphane ligands.

In the ^1H NMR spectra of **3a**,**b**, the resonances of the allylic methylene protons, which become diastereotopic due to the coordination of the ruthenium center, are now split into two doublets of doublets at δ = 5.80 and 4.76 ppm for **3a** and at δ = 6.20 and 4.21 ppm for **3b**, which requires *cis* coordination of the two chloro ligands. Recrystallization of **3a** from CH_2Cl_2/Et_2O resulted in the formation of single crystals suitable for X-ray analysis. As already indicated by the NMR spectra, the ruthenium centers were found in a distorted octahedral coordination environment with the tridentate N,N,N-ligand adopting a meridional geometry and the two chloro ligands in a *cis* arrangement (Figure 1). Compound **3a** crystallizes with two crystallographically independent units in the solid state. The structural parameters of these two units are almost identical (see the Supporting Information), therefore, we take just one of the two units for discussion of the geometry.

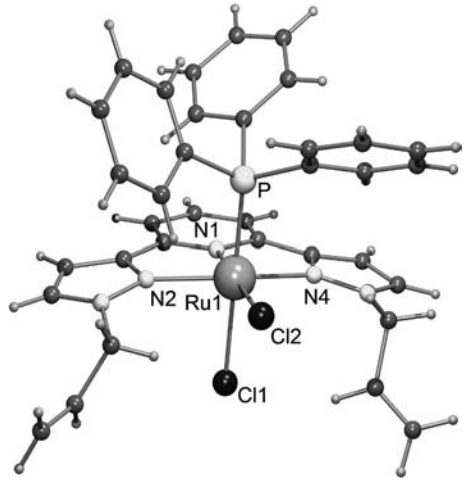


Figure 1. Molecular structure of the ruthenium(II) complex **3a** in the solid state. Characteristic bond lengths [Å] and angles [°] for one of the crystallographically independent units are given: Ru1–Cl1 2.4577(9), Ru1–Cl2 2.4665(8), Ru1–P1 2.2799(9), Ru1–N1 1.985(3), Ru1–N2 2.081(3), Ru1–N4 2.093(3), Cl1–Ru1–Cl2 88.99(3), Cl1–Ru1–P1 175.03(3), Cl1–Ru1–N1 90.40(7), Cl1–Ru1–N2 83.59(7), Cl1–Ru1–N4 89.00(7), Cl2–Ru1–P1 86.27(3), Cl2–Ru1–N1 178.65(8), Cl2–Ru1–N2 103.78(7), Cl2–Ru1–N4 100.71(7), P1–Ru1–N1 94.37(7), P1–Ru1–N2 96.08(7), P1–Ru1–N4 93.34(7), N1–Ru1–N2 77.35(10), N1–Ru1–N4 78.07(10), N2–Ru1–N4 154.24(10).

Although pyridines are generally considered to be better donors than pyrazoles, the large Ru–N bond length difference of about 10 pm can be explained simply by the steric requirements of the tridentate ligand.[19,20] Bidentate pyrazolylpyridine complexes show less-pronounced differences in the M–N bond lengths.[19,21] Due to the tridentate coordination of the N,N,N-donor, the central nitrogen atom, N1, is pushed closer to the ruthenium(II) center. It therefore applies a *trans* influence to Cl2 comparable to the *trans* influence of the phosphane donor to Cl1, which explains the almost identical Ru–Cl bond lengths found in this solid-state structure. All P–Ru–N angles are larger than 90°,

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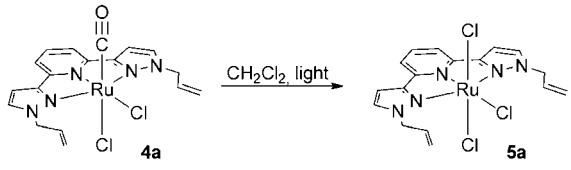
showing the steric influence of bulky triphenylphosphane on the chelating ligand.

Bubbling CO into a solution of **3a**,**b** in toluene at reflux results in the formation of the carbonyl complexes **4a**,**b** in quantitative yields (Scheme 1); a color change from red to yellow indicates the end of the reaction. The ^{31}P NMR spectroscopy signals of the triphenylphosphane ligands have disappeared, proving that the phosphane is substituted by CO, which is in contrast to previous findings.[19] The ^{1}H NMR spectra of **4a** and **4b** recorded in [D_6]DMSO again show two diastereotopic methylene protons (**4a**: δ = 6.12, 5.20 ppm; **4b**: δ = 5.55, 5.03 ppm), which means that the chloride ligands are still *cis* coordinated. In the ^{13}C NMR spectrum, the resonances of the carbonyl ligand are observed at δ = 191.01 ppm for **4a** and at δ = 191.22 ppm for **4b**. Intense CO absorptions in the infrared spectrum at 1936 cm^{-1} for **4a** and at 1948 cm^{-1} for **4b** confirm the attachment of one carbonyl ligand to the ruthenium center. The slight difference of 12 cm^{-1} can be explained by the steric influence of the bulky butyl chain attached to compound **4b**, which increases the Ru–CO distance, decreases back donation to the carbonyl ligand, and therefore, strengthens the C=O bond. Attempts to obtain single crystals of **4a** suitable for X-ray structure determination by recrystallization from dichloromethane over a long period of time and in the presence of light resulted in oxidation to ruthenium(III) and replacement of the carbonyl with a chloride ligand (Scheme 2 and Figure 2).



Scheme 2. Chlorination of the carbonyl complex **4a**.

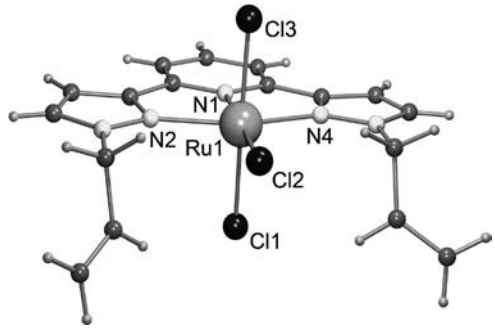


Figure 2. The molecular structure of the ruthenium(III) complex **5a** in the solid state, characteristic bond lengths [Å], and angles [°] are shown; the co-crystallized dichloromethane molecule is omitted for clarity. Ru1–Cl1 2.4159(18), Ru1–Cl2 2.405(5), Ru1–Cl3 2.358(2), Ru1–N1 2.039(5), Ru1–N2 2.089(5), Ru1–N4 2.043(5), Cl1–Ru1–Cl2 93.88(11), Cl1–Ru1–Cl3 177.59(6), Cl1–Ru1–N1 87.82(15), Cl1–Ru1–N2 89.66(15), Cl1–Ru1–N4 89.56(16), Cl2–Ru1–Cl3 87.79(12), Cl2–Ru1–N1 177.92(18), Cl2–Ru1–N2 101.86(18), Cl2–Ru1–N4 104.24(18), Cl3–Ru1–N1 90.55(16), Cl3–Ru1–N2 91.70(15), Cl3–Ru1–N4 88.34(16), N1–Ru1–N2 76.9(2), N1–Ru1–N4 77.0(2), N2–Ru1–N4 153.9(2).

As in **3a**, the ruthenium center in **5a** is again coordinated in a distorted octahedral geometry with the tridentate N,N,N-donor adopting a *mer* arrangement. The Ru–N bond on one side and the Ru–Cl distances on the other side are almost identical; slight differences are related to packing effects in the solid-state structure. The bond angle Cl3–Ru–N approaches 90°, corroborating the discussion of the steric influence of the triphenylphosphane ligand on the structure of **3a**.

Catalytic Transfer Hydrogenation

Acetophenone has been chosen as a model substrate to explore the catalytic performance of compounds **3** and **4** in transfer hydrogenation. The reaction conditions were optimized by first using **3a** (Table 1). Due to the poor solubility of the catalyst in 2-propanol, dichloromethane was added to obtain a homogeneous solution. All reactions were carried out at room temperature and the catalyst generally showed high activities even under these very mild conditions. It seemed that too much base and diluting the solution of the reaction reduced the reaction rate (entries 8 and 5, Table 1). As expected, the rate of the reaction increased dramatically by increasing the temperature (entry 7, Table 1). A blank experiment carried out in the absence of the catalyst gave no hydrogenation of acetophenone at all (entry 9, Table 1).

Table 1. Transfer hydrogenation of acetophenone with **3a**.[a]

Entry	Substrate/catalyst/base ratios			Solvent [mL]	Yield [%] after 0.5 h	1 h	1.5 h
1	200	1	–	25	0	0	0
2	200	1	1	25	92	93	94
3	200	1	2.5	25	88	92	92
4	200	1	5	25	73	87	99[b]
5	200	1	5	50	69	92	92
6	500	1	5	25	48	62	71
7[c]	200	1	5	25	100[d]	0	0
8	200	1	10	25	22	37	49
9	200	–	5	25	0	0	0[e]

[a] Reaction conditions: **3a** (2.5×10^{-2} mmol), 2-propanol (20 mL), CH_2Cl_2 (5 mL), room temp., N_2, monitored by GC. [b] Reaction completed after 80 min. [c] Reaction carried out at 82 °C. [d] Reaction completed after 5 min. [e] Even after about 3 h no product was detected without catalyst.

According to these results, the catalysis reactions were carried out by using a 0.5 M solution of the substrate, 0.5 mol-% of catalyst, and 0.025 M of KOH. For this purpose, a solution of the substrate in 2-propanol was added at room temperature to a solution in 2-propanol/CH_2Cl_2 containing the catalyst and the base. With the addition of the base, the color of the solution turned to a more intense red color, but during the reaction the color of the solution remained unchanged.

Complex **3a** was found to catalyze the reduction of acetophenone to 1-phenylethanol quantitatively in 80 min at room temperature. Substitution of the protons in the 5-position of the pyrazole ring with *n*-butyl groups dramatically increases the performance: in the presence of catalyst

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3b, the transformation is completed in less than 15 min at room temperature (Table 2), giving a minimum TOF of 800 h^{-1}. We assign this finding to an increase in steric hindrance by the *n*-butyl groups, which will force the allyl chains to be oriented away from the rear side of the catalyst. This will probably enable the dissociation of the triphenylphosphane ligand and activate the catalyst for the transfer hydrogenation process. This mechanistic idea is corroborated by replacing the triphenylphosphane ligand with a carbon monoxide ligand (compounds **4a**,**b**), which makes the catalyst almost inactive even at 82 °C.

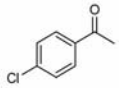
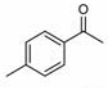
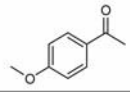
Table 2. Transfer hydrogenation of acetophenone with different ruthenium catalysts.[a]

Entry	Catalyst	Time [min]	Yield [%]
1	**3a**	80	99
2	**3b**	15	100
3	**4a**	1080	0
4	**4b**	1080	traces
5[b]	**4a**	60	0
		180	traces
6[b]	**4b**	60	13
		180	16

[a] Reaction conditions: catalyst (5×10^{-3} mmol), substrate (1.0 mmol), KOH (2.5×10^{-2} mmol), 2-propanol (4 mL), CH_2Cl_2 (1 mL), room temp., N_2, monitored by GC. [b] Reaction carried out at 82 °C.

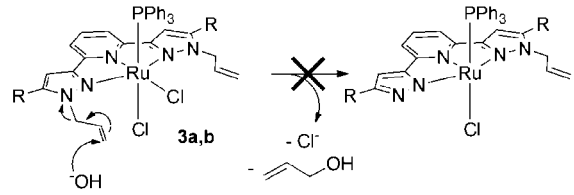
Finally the activity of **3b** was tested with a few different ketones to show its general applicability in transfer hydrogenation (Table 3). The results prove that increasing the electron density at the aromatic ring reduces the reaction rate. Complete conversion for the first two substrates was observed after 10 min at room temperature resulting in a minimum TOF of 1200 h^{-1}.

Table 3. Transfer hydrogenation of different ketones with **3b**[a].

Entry	Substrate	Yield [%]
1		100
2		100
3		96
4		51

[a] Reaction conditions: substrate (1.0 mmol), **3b** (5×10^{-3} mmol), KOH (2.5×10^{-2} mmol), 2-propanol (4 mL), CH_2Cl_2 (1 mL), room temp., N_2, reactions monitored by GC, samples were taken after 10 min.

Concerning the mechanism of the transfer hydrogenation catalyzed by **3a**,**b**, we suggest a reaction sequence following an inner coordination of the substrate. We have no evidence for a ligand-assisted process, which could be initiated by splitting one or both of the allylic chains through an S_N2 or S_N2' reaction with the base leading to an anionic pyrazolate donor (Scheme 3) and a vacant coordination site at the ruthenium(II) center. This reaction would generate an intermediate suitable for a ligand-assisted, outer-coordination mechanism.



Scheme 3. Cleavage of the allyl–N bond by the base.

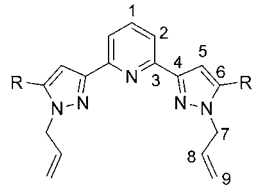
Treatment of **3a**,**b** with KOH did not result in cleavage of the N–allyl bond. Cleaving the Ru–P bond, further promoted by the steric demand of the butyl chain in complex **3b**, should therefore be the initial step to generate a reactive 16-VE ruthenium(II) species, which then leads to the formation of the catalytically active ruthenium hydride species. This is supported by the fact that addition of an excess of PPh_3 to the catalyst strongly decreases the reaction rates of **3a**,**b**, which is similar to findings reported in the literature.[22] Comparing the activity of **3b** (TOF $\geq$ 1200 h^{-1}) at room temperature makes it clear that we have obtained a highly active structural motif. It already had been shown in the literature that ruthenium(II) complexes with *trans*-coordinated chloro ligands are less active in the transfer hydrogenation of ketones than ruthenium(II) complexes with *cis*-coordinated chloro ligands (such as **3a**,**b**).[18a,18b,23]

Conclusions

We have described new ruthenium complexes of the type $[RuCl_2(L)(NNN)]$ with tridentate dipyrazolylpyridine N,N,N-ligands. The triphenylphosphane complexes turned out to be highly efficient catalyst precursors for the transfer hydrogenation of aromatic ketones. The introduction of a butyl group in the 5-positions of the pyrazoles led to a pronounced increase in catalytic activity.

Experimental Section

General: Solvents were purified and dried by standard methods. All reactions were carried out under an atmosphere of dinitrogen. The ligand precursors **1a** and the ruthenium(II) complex $[RuCl_2(PPh_3)_3]$ were synthesized according to procedures published in the literature.[16a,24] The NMR spectra are assigned according to Scheme 4.



Scheme 4. Atom numbering used for NMR signal assignments.

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2,6-Bis(5-butyl-1*H*-pyrazol-3-yl)pyridine (1b): A solution of hexan-2-one (15.41 g, 154 mmol) in dry THF (40 mL) was added at room temperature dropwise to a solution of pyridine-2,6-dicarboxylicacid dimethylester (15 g, 76.9 mmol) and NaOMe (8.35 g, 154 mmol) in dry THF (170 mL). Then, the reaction mixture was heated for 5 h to reflux. After cooling to room temperature, the solvent was evaporated under vacuum and the resulting orange colored solid was dissolved in a 1:1 mixture of chloroform (100 mL) and water (100 mL). While vigorously stirring the reaction mixture, 1 M sulfuric acid was added until a pH value of 5 was reached. The organic phase was separated, washed three times with water (50 mL), and then dried with Na_2SO_4. After the solvent was removed in vacuo, a light-brown oil resulted, which was dissolved in ethanol (200 mL) and reacted for 4 h under reflux conditions with $N_2H_4{\cdot}H_2O$ (8.86 g, 177 mmol). The solvent and the excess hydrazine were removed in vacuo and the light-yellow solid product was recrystallized from ethyl acetate (15 g, 60%). $C_{19}H_{25}N_5$ (323.44): calcd. C 70.56, H 7.79, N 21.65; found C 70.60, H 7.70, N 21.70. ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C): δ = 7.43 (t, J_{HH} = 7.43 Hz, 1 H, H1), 7.20 (br. s, 2 H, H2), 6.25 (br. s, 2 H, H5), 2.50 (br. s, 4 H, H_{bu}), 1.52 (m, 4 H, H_{bu}), 1.29–1.23 (m, 4 H, H_{bu}), 0.81 (t, J_{HH} = 7.44 Hz, 6 H, H_{bu}) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 153.0 (s, C3), 148.3 (s, C1), 144.3 (s, C4), 137.0 (s, C6), 117.8 (s, C2), 101.4 (s, C5), 31.6 (s, C_{bu}), 27.3 (s, C_{bu}), 22.7 (s, C_{bu}), 14.0 (s, C_{bu}) ppm.

2,6-Bis(1-allyl-1*H*-pyrazol-3-yl)pyridine (2a): LiH (0.16 g, 20 mmol) was added to a solution of **1a** (2.1 g, 10 mmol) in dry THF (75 mL). After the evolution of dihydrogen ceased, allylic bromide (1.2 g, 20 mmol) was added and the reaction mixture and was stirred for 12 h. After removing the solvent in vacuo, the product was extracted with chloroform and the organic phase was filtered through sodium sulfate. Removing the solvent under reduced pressure gave the product as a pale-yellow solid (1.9 g, 65%). $C_{17}H_{17}N_5$ (291.35): calcd. C 70.08, H 5.88, N 24.04; found C 70.82, H 5.74, N 23.44. ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C): δ = 8.22 (br. s, 2 H, H2), 7.86 (br. s, 1 H, H1), 7.75 (d, J_{HH} = 2.35 Hz, 2 H, H5), 7.55 (d, J_{HH} = 2.35 Hz, 2 H, H6), 6.08–5.98 (m, 2 H, H8), 5.31–5.24 (m, 4 H, H9,H10), 4.85 (d, J_{HH} = 5.87 Hz, 4 H, H7) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 147.9 (s, C3), 144. 8 (s, C4), 143.3 (s, C1), 132.0 (s, C8), 131.7 (s, C6), 121.4 (s, C2), 119.7 (s, C9), 108. 9 (s, C5), 55.4 (s, C7) ppm.

2,6-Bis(1-allyl-5-butyl-1*H*-pyrazol-3-yl)pyridine (2b): The same procedure as that used for **2a** was applied to give **2b** as a pale-yellow solid (2.8 g, 70%,). $C_{25}H_{33}N_5$ (403.57): calcd. C 74.40, H 8.24, N 17.35; found C 74.29, H 8.25, N 17.40. ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C): δ = 7.79 (d, J_{HH} = 7.83 Hz, 2 H, H2), 7.59 (t, J_{HH} = 7.82 Hz, 1 H, H1), 6.76 (s, 2 H, H5), 5.95–5.82 (m, 2 H, H8), 5.05 (d, J_{HH} = 10.17 Hz, 2 H, H9), 4.88 (d, J_{HH} = 17.22 Hz, 2 H, H10), 4.62 (br. s, 4 H, H7), 2.46 (t, J_{HH} = 7.83 Hz, 4 H, H_{bu}), 1.61–1.54 (m, 4 H, H_{bu}), 1.35–1.26 (m, 4 H, H_{bu}), 0.84 (t, J_{HH} = 7.43 Hz, 6 H, H_{bu}) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 151.8 (s, C3), 150.7 (s, C4), 144.4 (s, C1), 136.5 (s, C6), 133.1 (s, C8), 117.9 (s, C2), 116.5 (s, C9), 103.1 (s, C5), 51.6 (s, C7), 30.2 (s, C_{bu}), 24.9 (s, C_{bu}), 22.1 (s, C_{bu}), 13.6 (s, C_{bu}) ppm.

[2,6-Bis(1-allyl-1*H*-pyrazol-3-yl)pyridine]dichloro(triphenylphosphane)ruthenium(II) (3a): Compound **2a** (0.15 g, 0.37 mmol) was added to a solution of $[RuCl_2(PPh_3)_3]$ (0.355 g, 0.37 mmol) in dry CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for about 2 h. After concentrating the solution to about 5 mL, dry diethyl ether (25 mL) was added to precipitate the product, which was filtered off and washed with diethyl ether to remove liberated triphenylphosphane to give the final product as a red solid (0.268 g, 100%). $C_{35}H_{32}Cl_2N_5PRu$ (725.62): calcd. C 57.93, H 4.45, N 9.65; found C 57.64, H 4.45, N 9.65. ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C): δ = 7.35 (d, J_{HH} = 2.72 Hz, 2 H, H6), 7.29 (t, J_{HH} = 7.49 Hz, 1 H, H1), 7.25–7.18 (m, 5 H, H2,H_{Ph}), 7.09–7.06 (m, 12 H, H_{Ph}), 6.75 (d, J_{HH} = 2.72 Hz, 2 H, H5), 6.15–6.04 (m, 2 H, H8), 5.80 (dd, 4 H, H7), 5.32 (m, 4 H, H9,H10), 4.76 (dd, 2 H, H7) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 155.8 (s, C1), 152.6 (s, C4), 134.1 (d, J_{CP} = 41.62 Hz, C_{ph}), 133.4 (d, J_{CP} = 9.24 Hz, C_{ph}), 133.0 (s, C8), 132.5 (s, C6), 132.0 (s, C3), 129.0 (br. s, C_{ph}), 127.8 (d, J_{CP} = 8.33 Hz, C_{ph}), 120.2 (s, C2), 116.9 (s, C9), 105.5 (s, C5), 56.2 (s, C7) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 20 °C): δ = 44.2 ppm.

[2,6-Bis(1-allyl-5-butyl-1*H*-pyrazol-3-yl)pyridine]dichloro(triphenylphosphane)ruthenium(II) (3b): The same procedure as that used for **3a** was applied to give **3b** as a red solid (0.31 g, 100%). $C_{43}H_{48}Cl_2N_5PRu$ (837.84): calcd. C 61.67, H 5.73, N 8.36; found C 61.95, H 5.68, N 7.68. ^{1}H NMR (400.1 MHz, $CDCl_3$, 20 °C): δ = 7.34 (t, J_{HH} = 8.22 Hz, 1 H, H1), 7.21 (m, 3 H, H_{ph}), 7.15 (d, J_{HH} = 7.44 Hz, 2 H, H2), 7.11–7.07 (m, 12 H, H_{Ph}), 6.47 (s, 2 H, H5), 6.22–6.19 (m, 4 H, H7,H8), 5.14–5.10 (m, 4 H, H9,H10), 4.24–4.18 (m, 2 H, H7), 2.59–2.54 (m, 4 H, H_{bu}), 1.60–1.56 (m, 4 H, H_{bu}), 1.39–1.34 (m, 4 H, H_{bu}), 0.94 (t, J_{HH} = 7.05 Hz, 6 H, H_{bu}). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 156.2 (s, C1), 151.6 (s, C4), 148.0 (s, C3), 134.5 (d, J_{CP} = 40.69 Hz, C_{ph}), 134.4 (s, C8), 133.4 (d, J_{CP} = 9.24 Hz, C_{ph}), 131.8 (s, C6), 128.8 (br. s, C_{ph}), 127.6 (d, J_{CP} = 9.25 Hz, C_{ph}), 117.6 (s, C2), 116.5 (s, C9), 104.0 (s, C5), 53.8 (s, C7), 30.1 (s, C_{bu}), 25.8 (s, C_{bu}), 22.4 (s, C_{bu}), 14.00 (s, C_{bu}). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 20 °C): δ = 42.7 ppm.

[2,6-Bis(1-allyl-1*H*-pyrazol-3-yl)pyridine]carbonyldichlororuthenium(II) (4a): Compound **3a** (0.145 g, 0.2 mmol) was dissolved in dry toluene/CH_2Cl_2 (10:1) and CO gas was bubbled into the solution heated at reflux. The color of the solution changed from red to yellow. When the reaction mixture cooled to room temperature, a yellow powder precipitated, which was filtered off washed with dry diethyl ether to give the product as a yellow solid (0.098 g, 100%). $C_{18}H_{17}Cl_2N_5ORu{\cdot}CH_2Cl_2$: calcd. C 39.60, H 3.32, N 12.15; found C 40.05, H 3.56, N 12.33. ^{1}H NMR (400.1 MHz, [D_6]-DMSO, 20 °C): δ = 8.21–8.10 (m, 5 H, H1,H2,H6), 7.36 (d, J_{HH} = 2.19 Hz, 2 H, H5), 6.16–6.09 (m, 2 H, H8), 5.51–5.47 (dd, 2 H, H7), 5.23–5.19 (m, 6 H, H7,H9,H10) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, [D_6]DMSO, 20 °C): δ = 191.0 (s, CO), 152.8 (s, C3), 152.3 (s, C4), 138.8 (s, C8), 135. (s, C6), 133.7 (s, C1), 119.2 (s, C2), 118.3 (s, C9), 106.7 (s, C5), 53.9 (s, C7) ppm. IR (KBr): $\tilde{\nu}$ = 1936 (C=O) cm^{-1}.

[2,6-Bis(1-allyl-1*H*-pyrazol-3-yl)pyridine]carbonyldichlororuthenium(II) (4b): The same procedure as that used for **4a** was applied to give **4b** as a yellow solid (0.121 g, 100%). $C_{26}H_{33}Cl_2N_5ORu$ (603.56): calcd. C 51.74, H 5.51, N 11.60; found C 50.73, H 5.54, N 11.60. ^{1}H NMR (400.1 MHz, [D_6]DMSO, 20 °C): δ = 8.15 (t, J_{HH} = 7.49 Hz, 1 H, H1), 8.05 (d, J_{HH} = 7.83 Hz, 2 H, H2), 7.21 (s, 2 H, H5), 6.05–5.96 (m, 2 H, H8), 5.58 (dd, 2 H, H7), 5.19 (dd, 4 H, H9,H10), 5.07 (d, J_{HH} = 17.37 Hz, 2 H, H7), 2.76–2.66 (m, 4 H, H_{bu}), 1.70–1.62 (m, 4 H, H_{bu}), 1.43–1.36 (m, 4 H, H_{bu}), 0.96–0.91 (m, 6 H, H_{bu}) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz [D_6]DMSO, 20 °C): δ = 191.2 (s, CO), 153.0 (s, C3), 151.4 (s, C4), 148.3 (d, C6), 138.8 (s, C8), 133.3 (s, C1), 119.0 (s, C2), 117.1 (s, C9), 105.0 (s, C5), 51.3 (s, C7), 29.3 (s, C_{bu}), 24.7 (s, C_{bu}), 21.8 (s, C_{bu}), 13.7 (s, C_{bu}) ppm. IR (KBr): $\tilde{\nu}$ = 1948 (C=O) cm^{-1}.

General Procedure for the Catalytic Transfer Hydrogenation: Solutions containing the substrate (a), the catalyst (b), and KOH (c) were prepared as follows: (a) the organic substrate (5 mmol) was dissolved in 2-propanol (10 mL), (b) the ruthenium complex

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(0.025 mmol) was dissolved in 2-propanol (5 mL) and CH_2Cl_2 (5 mL), and (c) KOH (0.125 mmol) was dissolved in 2-propanol (5 mL). Solution (c) was added to solution (b), then solution (c) was added to this mixture. The reactions were monitored by GC.

X-ray Structure Analyses: Crystal data and refinement parameters for compounds **3a** and **5a** are collected in Table 4. The structures were solved by direct methods (SIR92[25]), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.[26] For **3a** and **5a**, semi-empirical absorption corrections from equivalents (Multiscan) were carried out.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined by using a riding model.

Table 4. Summary of the crystallographic data and details of data collection and refinement.

	3a	**5a**
Empirical formula	$C_{35}H_{32}Cl_2N_5PRu$	$C_{18}H_{19}Cl_5N_5Ru$
Formula weight	725.60	583.70
Crystal size [mm]	$0.19 \times 0.17 \times 0.06$	$0.20 \times 0.13 \times 0.03$
T [K]	150(2)	150(2)
λ [Å]	1.54184	1.54184
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	13.0148(9)	8.0575(4)
b [Å]	14.8928(10)	10.4714(4)
c [Å]	16.8628(10)	14.3250(7)
α [°]	102.805(6)	71.813(4)
β [°]	92.194(5)	81.249(4)
γ [°]	93.225(5)	76.049(4)
V [Å^3]	3177.8(4)	1110.51(9)
Z	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.517	1.746
μ [mm^{-1}]	6.280	11.381
θ-range [°]	3.41–62.92	3.26–62.60
Reflections collected	27114	8213
Independent reflections	9952 [R_{int} = 0.0352]	3539 [R_{int} = 0.0252]
Data/restr./parameters	9952/0/793	3539/0/262
Final R indices $[I > 2\sigma(I)]$[a]	0.0299, 0.0787	0.0556, 0.1596
R indices (all data)	0.0362, 0.0823	0.0595, 0.1626
GooF[b]	0.985	1.096
$\Delta\rho_{max/min}$ [e Å^{-3}]	0.880/–0.749	1.573/–1.549

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $\omega R2 = [\Sigma\omega(F_o^2 - F_c^2)2/\Sigma\omega F_o^2]^{1/2}$. [b] GooF $= [\Sigma\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$.

CCDC-823928 (for **3a**) and -823929 (for **5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): NMR and IR spectra.

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