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Probing the effect of heterocycle-bonding in PNX-type ruthenium pre-catalysts for reactions involving H_2

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A series of ruthenium(II) complexes with three novel PNX-type pincer ligands is reported, in which X denotes a heterocyclic donor group (PNX = $Ph_2PCH_2CH_2N(H)CH_2$-X, X = 2-pyridyl, 2-furanyl, 2-thiophenyl or 2-pyrrolyl). The reaction of $[(Ph_3P)_3RuCl_2]$ with one equivalent of ligand leads to the trans-dichloro complexes $[(PNX)RuCl_2(PPh_3)]$ (**1**-**4**) for all ligands, whereas the complexation of $[(Ph_3P)_3Ru(H)(Cl)(CO)]$ results in different type of complexes. The variation of the heterocyclic donor group is in line with different binding properties and a labilization of this group. Investigations on the catalytic activity of different types of ruthenium(II) complexes in hydrogenation and dehydrogenation reactions reveal that more labile bound heterocycle donors result in a decrease of catalytic productivity and activity.

Introduction

Catalytic hydrogenation reactions of carbonyl compounds have gained increased importance for the production of bulk chemicals, ranging from flavour molecules to pharmaceutical building blocks.[1-5] With the aim to replace stoichiometric reducing reagents,[6] such as $NaBH_4$ or $LiAlH_4$, by more atom economical catalytic hydrogenation reactions, a large variety of homogenous ruthenium catalysts have been developed.[5, 7-10] Most prominently, the chiral diphosphine-diamine-based ruthenium complexes, originally reported by *Noyori* and co-workers, were applied to various pro-chiral substrates.[8, 9]

While most investigations are focused on asymmetric hydrogenations, only little attention has been paid to achiral hydrogenation reactions of carbonyl compounds, which are potentially having an even wider scope.[11, 12] Thus, in continuation of the work on diamine-diphosphine-based catalysts different ruthenium complexes bearing P,N-ligands have been reported as catalysts for hydrogenation and dehydrogenation reactions.[12, 13] The utilization of pincer-type ligands in combination with an ancillary ligand turned out to be very successful for catalytic hydrogenations of challenging substrates such as esters, amides or carbonates.[14-16] Thereby PNN-type complexes, containing two N-donor groups in addition to a tertiary phosphine group, exhibit particular high activities.

In addition to a cooperative side that reversibly provides a proton, arm-opening of one of the two terminal donor-groups of the pincer ligand has been discussed to be responsible for the high catalytic activity of some of these complexes.[17, 18] This reversible de-coordination of a donor-group, often named hemilability, allows for the generation of a vacant coordination side within a possible catalytic cycle. Weakening of the bond between the central ruthenium atom and the third donor group could increase the hemilability and therewith possibly the catalytic activity. Following this approach, we decided to modify a known pincer-type ligand with a pyridine ring as third donor group ($\mathbf{L_1}$, Scheme 1), that has originally been used by *Gusev* and co-workers in highly active ruthenium and osmium catalysts for hydrogenation and dehydrogenation reactions.[19-21] Importantly, for ruthenium and osmium catalysts with these kind of ligands, reversible de-coordination of the pyridine-arm has been considered as a likely event during the catalytic cycle.[19, 21] For this reason, the exchange of the pyridine arm in $\mathbf{L_1}$ by less coordinating heterocycles seems a promising approach that could provide further evidence for the proposed mechanism. Herein, we present our investigations with a series of ruthenium complexes containing PNX-type ligands ($\mathbf{L_1}$-$\mathbf{L_4}$), in which X denotes a heterocyclic donor ligand.

Results and discussion

Ligand and complex synthesis

Following the procedure by *Gusev* and co-workers for the ligand $\mathbf{L_1}$ we were able to synthesize the novel ligands $\mathbf{L_2}$-$\mathbf{L_4}$ by condensation of readily available (2-aminoethyl)diphenylphosphine with a heterocyclic aldehyde and *in situ* reduction of the generated imine with $NaBH_4$ (Scheme 1).[19] While in ligands $\mathbf{L_1}$-$\mathbf{L_3}$ only the electronic properties of the third donating group are varied, the pyrrole ring in ligand $\mathbf{L_4}$ represents an additional proton source.

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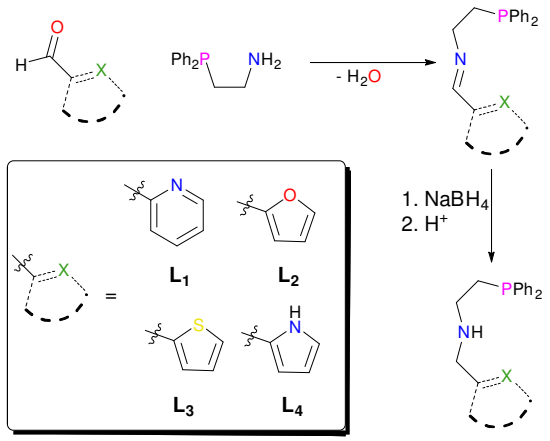
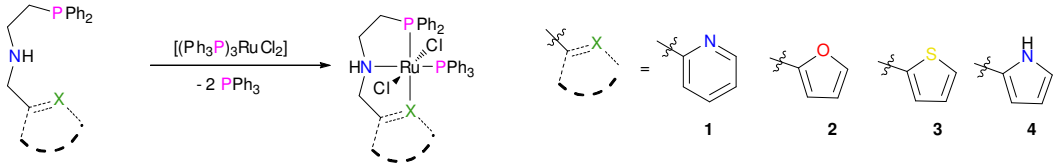
† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of the ligands $\mathbf{L_1}$-$\mathbf{L_4}$.

With the aim to synthesize suitable pre-catalysts, all ligands were reacted with different ruthenium precursors. In case of the ligand $\mathbf{L_1}$, the reaction with one equivalent of $[(Ph_3P)_3RuCl_2]$ has been previously reported to result in the formation of *trans*-$[(L_1)RuCl_2(PPh_3)]$ (**1**). In this octahedral complex the ancillary PPh_3 ligand and pincer ligand form a plane, while the two chloro ligands occupy the apical positions. Interestingly, the analogous reactions with $\mathbf{L_2}$-$\mathbf{L_4}$ lead to the same type of complexes (**2**-**4**), which has been confirmed by single crystal X-ray diffraction and multinuclear NMR spectroscopy (Scheme 2). A closer look on the molecular structures (Figure 1) revealed, that the ruthenium phosphorus bond length of the PPh_2-group is significantly influenced by the heterocyclic donor in *trans*-position. Pyridine, as a rather electron deficient heterocycle with σ-donor and π-acceptor properties, causes a decrease of π-back bonding from the PPh_2-group in *trans* position to the central ruthenium atom, which is reflected in a slightly elongated Ru-P bond in complex **1** (2.3022 Å). In comparison, furan is a much weaker σ-donor that rather acts as a π-donor. Accordingly, the corresponding ruthenium phosphorus bond is significantly shorter in complex **2** (2.2216 Å). The corresponding bond lengths in complex **3** (2.611 Å) and **4** (2.2902 Å) are between those observed in **1** and **2**. A similar trend is observed for the chemical shifts in the $^{31}P\{^1H\}$ NMR spectra corresponding to the PPh_2-group. The weak donor abilities of the heterocycles in *trans* position to the Ph_2P-groups are reflected in a down field shift of the resonance corresponding to the Ph_2P-groups in the $^{31}P\{^1H\}$ NMR spectrum. Thereby the weak bonding of the heterocycle causes a stronger σ-donation of the Ph_2P-groups in *trans*-position and therewith a decreased electron density at the corresponding phosphorus atom.[22] In line with the observed ruthenium phosphorus bond length, complexes **1** and **4** give rise to a doublet resonance at 49.1 ppm and 51.0 ppm in the $^{31}P\{^1H\}$NMR spectrum, respectively, whereas downfield shifted resonances are observed for complex **2** at 81.5 ppm and complex **3** at 63.2 ppm.



Scheme 2. Synthesis of complexes **1**-**4** using $[(Ph_3P)_3RuCl_2]$.

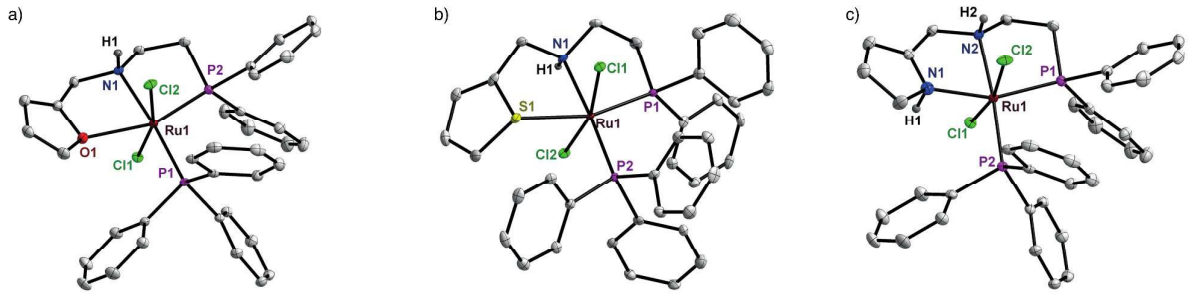


Figure 1. ORTEP diagram of complexes **2**-**4** with the thermal ellipsoids set at 50% probability (selected hydrogen atoms and solvent molecules were omitted for clarity).

Contrary to the observations made with $[(Ph_3P)_3RuCl_2]$, the reaction with one equivalent of $[(Ph_3P)_3Ru(H)(Cl)(CO)]$ results in a different type of complex for $\mathbf{L_1}$ than for $\mathbf{L_2}$-$\mathbf{L_4}$. In case of the pyridine-based ligand $\mathbf{L_1}$ the formation of the cationic hydrido carbonyl complex $[(L_1)Ru(H)(CO)(PPh_3)]Cl$ **5** (Scheme 3). Complex **5** is coordinated by one deprotonated PNN-ligand in a facial fashion, by one hydride, one carbonyl and one triphenylphosphine ligand. In contrast, the reaction under identical conditions with $\mathbf{L_2}$-$\mathbf{L_4}$ leads to the ruthenium hydrido chloro carbonyl complexes **6**-**8**. In these complexes one additional PPh_3 ligand coordinates to the central ruthenium atom, causing a κ^2-coordination of the pincer-type ligand. The κ^2-coordination in favor of the κ^3-coordination without the ancillary PPh_3 ligand, again indicates a weaker bonding of the heterocyclic thiophen, furan and pyrrole groups in $\mathbf{L_2}$-$\mathbf{L_4}$.

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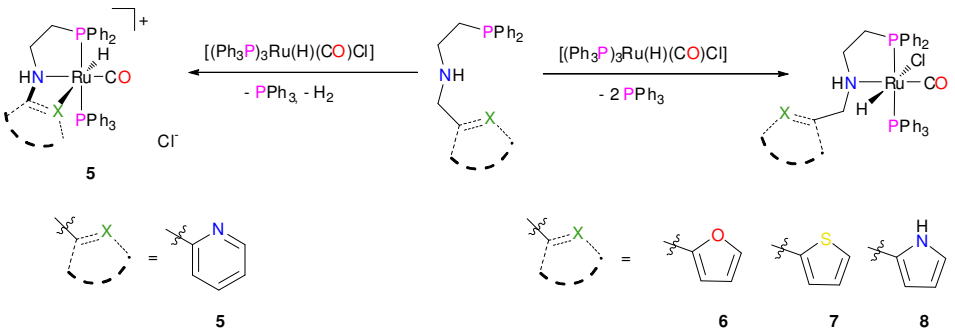


Scheme 3. Synthesis of complexes **5**-**8** using $[(Ph_3P)_3Ru(H)(Cl)(CO)]$.

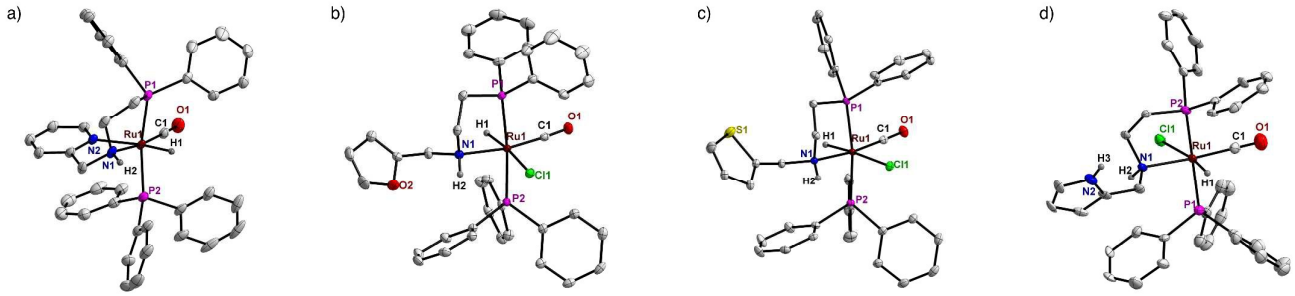
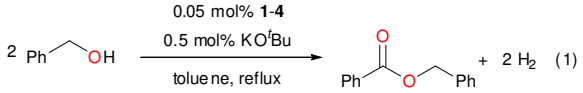


Figure 2. ORTEP diagram of complexes **5**-**8** with the thermal ellipsoids set at 50% probability (selected hydrogen atoms, counter ions and solent molecules were omitted for clarity).

Catalysis

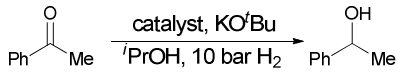
As ruthenium complexes with ligand $\mathbf{L_1}$ were reported to efficiently catalyze the dehydrogenation of primary alcohols to esters under liberation of H_2, as well as the reverse reaction, the hydrogenation esters to alcohols, we started to investigate the effect of the heterocyclic group on the catalytic activity in reactions involving dihydrogen. Furthermore, ruthenium complexes with analogous NNC-type ligands, where the Ph_2P-groups are replaced by carbene donor-groups were shown to be active pre-catalysts for the hydrogenation of ketones.[23] In preliminary experiments, we applied 0.05 mol% of complexes **1**-**4** as catalysts in the presence of 0.5 mol% KO^tBu in the acceptorless dehydrogenation of benzyl alcohol (reaction 1). With complex **1**, which is known as a highly active catalyst for the dehydrogenation of ethanol, benzyl benzoate was obtained in 60.5 % yield after 8 h. The utilization of complexes **2**-**4** as catalysts under otherwise identical conditions results in very poor conversions, with yields of 2.6 % in case of **2**, 7.0 % in case of **3** and less than 0.1 % for **4**. Apparently, the more weakly bound heterocyclic donor group in complexes **2**-**4** limits catalytic activity in these dehydrogenation reactions.



To further explore the catalytic potential, we investigated complexes **1**-**8** as catalysts in the hydrogenation of different substrates. As the complexes showed only poor activity in the hydrogenation of different esters, we utilized them as pre-catalysts for the hydrogenation of ketones. Therefor, different reaction parameters such as the nature and amount of base, the solvent and temperature were optimized for acetophenone, a commonly used test substrate. It should be noted that the best activities were observed in protic solvents such as ethanol or 2-propanol, whereas in polar aprotic solvents or under neat conditions the activity is significantly decreased. In addition, we proved that with ^{i}PrOH as solvent at 60 °C the H_2 gas is the main source for hydrogenation, whereas at ambient temperature we could show by experiments in the absence of H_2, that transfer-hydrogenation is at least a competing pathway. However, using ethanol as solvent, which was proven by suitable control experiments not to act as H_2 source in the present case, almost identical activities were obtained in the hydrogenation of acetophenone. Selected experiments using 0.01

mol% catalyst, 8 mol% KO^{t}Bu under 10 bar of H_2 pressure in ^{i}PrOH as solvent are outlined in table 1 (Entry 1-8). The pyridine-based pre-catalyst **1** exhibits a high activity, leading to full conversion after one hour and the formation 1-phenylethanol in 99.7 % yield after 1 h at 60 °C (Entry 1). In contrast, with 21.8 % yield the catalytic activity of the furan-based catalyst **2** is significantly reduced in comparison (Entry 2), whereas the analogous thiophene-based complex **3** is comparable in productivity and activity to complex **1** (Entry 3). The pyrrole-based pre-catalyst **4** showed good catalytic activity as well, yielding 1-phenylethanol in 69.1 % yield (Entry 4). Complexes **5** and **6**-**8**, which are all having two ancillary ligands, CO and PPh_3, respectively, exhibit very similar activities in the hydrogenation reactions and give rise to very low yields (Entry 5-8). In experiments with lower catalyst loadings of 0.0005 mol% a turnover number of 67800 was obtained for complex **1**, whereas complex **3** gives rise to a turnover number of 46200 (Entry 9-10). Interestingly, at ambient temperature using 0.0025 mol% of pre-catalysts **1**-**4** and prolonged reaction times of 18 h the yield of 1-phenylethanol was more than 90 % for all four complexes (Entry 11-14).

Table 1. Hydrogenation of acetophenone.[a]

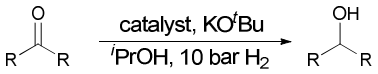


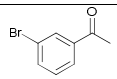
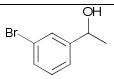
Entry	Cat.	S/B/C[b]	Conv./%	Yield/%[c]	TON[c]	TOF/h^{-1}
1	**1**	10000/800/1	>99.9	99.7	9970	9970
2	**2**	10000/800/1	24.8	21.8	2180	2180
3	**3**	10000/800/1	>99.9	99.8	9980	9980
4	**4**	10000/800/1	69.6	69.1	6910	6910
5	**5**	10000/800/1	9.7	6.9	690	690
6	**6**	10000/800/1	7.1	3.2	320	320
7	**7**	10000/800/1	5.2	4.2	420	420
8	**8**	10000/800/1	10.2	3.0	300	300
9[d]	**1**	200000/800/1	45.6	33.9	67800	3767
10[d]	**3**	200000/800/1	40.7	23.1	46200	2565
11	**1**	40000/800/1	95.1	94.5	37800	2100
12	**2**	40000/800/1	98.9	98.6	39400	2191
13	**3**	40000/800/1	92.7	92.2	36880	2049
14	**4**	40000/800/1	93.9	92.7	37080	2060

[a]Reaction conditions: acetophenone (5.00 mmol), catalyst (0.50 µmol), KO^{t}Bu (0.40 mmol), *m*-xylene (1.00 mmol), H_2 (10 bar) in ^{i}PrOH (3.00 ml) at 60 °C for 1 h; [b] S/BC = ratio of substrate/base/catalyst; [c]the conversion and yield was monitored by GC analysis with *m*-Xylene (1.00 mmol) as internal standard. [d]acetophenone (10.00 mmol) and catalyst (0.05 µmol) were used instead; [d]acetophenone (10.00 mmol) and catalyst (0.05 µmol) were used instead.

With the aim to extend the scope of our study and to address selectivity issues, we investigated the most active pre-catalysts among this series in the hydrogenation of various substrates. Although prolonged reaction times were required, in case of complex **1**, a bromo-substituent had only little impact on the yield of the corresponding alcohol (Table 2, Entry 1), while with complex **3** the productivity is reduced with a yield of 48.8 % (Entry 2). 2-Acetylpyridine, which can potentially bind to the central ruthenium atom, was hydrogenated in good yield with complex **1** as catalyst (Entry 3), whereas complex **3** showed no activity at all (Entry 4). This is likely due to strong substrate binding and thus provides further evidence for weaker binding of the thiophene-arm in **3** in comparison to the pyridine-arm in **1**. Benzophenone is hydrogenated only in poor yield by both catalysts(Entries 5 and 6). Aldehydes, such as benzaldehyde are rapidly hydrogenated with complex **1** as pre-catalyst (Entry 7), whereas complex **3** exhibits again much lower activities (Entry 8). However, cyclohexanone was hydrogenated excellent yields (Entries 9 and 10). The diastereoselective hydrogenation of norcamphor afforded *endo*-norborneol in 96.6 % yield as major product, using 0.2 mol% of complex **1** as pre-catalyst (Entry 11). With complex **3** as pre-catalyst the hydrogenation of norcamphor is complete after one hour too, but with 89.5 % yield of *endo*-norborneol the selectivity is slightly lower (Entry 12). The reduction of α,β-unsaturated ketones such as *trans*-4-phenyl-3-buten-2-one proceeds with selective hydrogenation of the C=O double bond and formation of the corresponding allyl alcohol in 98.8 % yield, with complex **1** as catalyst. Notably, turnover frequencies of 9880 h^{-1} were reached with this pre-catalyst, which is the highest value reported so far (Scheme 4).[11, 12, 24-31] With complex **3** as pre-catalyst only a slightly lower conversion of *trans*-4-phenyl-3-buten-2-one was obtained, but the C=O selectivity of the reduction was quite low. Thus, the desired allyl alcohol was formed only in 37.2 % yield, whereas the yield of the saturated alcohol was found to be 39.2 % and of saturated ketone 18.8 %.

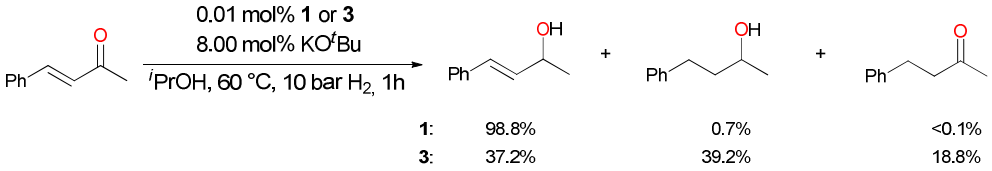
Table 2. Hydrogenation of aldehydes and ketones.



Entry	Substrate	Product	Catalyst	Time/h	Conversion/%[b]	Yield/%[b]	TON	TOF/h^{-1}
1[c]			**1**	18	>99.9	98.0	39200	2160
2[c]			**3**	18	58.1	48.4	19360	1076
3			**1**	2	62.3	47.1	4710	2355
4			**3**	2	0	0	-	-
5			**1**	18	9.2	8.4	840	47
6			**3**	18	19.0	18.3	1830	102
7			**1**	$^1/_3$	>99.9	99.1	9910	29730
8[d]			**3**	$^1/_3$	14.1	10.4	1040	3120
9			**1**	1	>99.9	99.9	9990	9990
10			**3**	1	>99.9	98.1	9810	9810

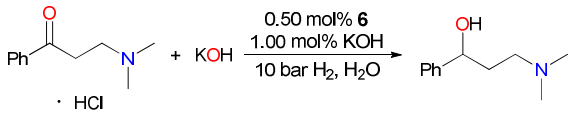
11[e]		 (endo) + (exo)	**1**	1	>99.9	96.6(*endo*)	3.3(*exo*)	499	499
12[e]			**3**	1	>99.9	89.5(*endo*)	10.4(*exo*)	499	499

[a]Reaction conditions: substrate (5.00 mmol), catalyst (0.50 µmol), KO^{t}Bu (8.00 mol %), *m*-xylene (1.00 mmol), H_2 (10 bar) in ^{i}PrOH (3.00 ml) at 60 °C. [b]The conversion and yield was monitored by GC analysis with *m*-xylene (1.00 mmol) as internal standard. For norcamphor, the conformation of two isomer products was further determined by ^{1}H NMR analysis. [c]Ketone (5.00 mmol) and catalyst (0.125 µmol) were used instead; [d]norcamphor (5.00 mmol) and Ru-cat. (0.01 mmol) were used under otherwise identical conditions.



Scheme 4. Hydrogenation of *trans*-4-phenyl-3-buten-2-one catalyzed by complexes **1** or **3**.

With the aim to develop a protocol for the catalytic reduction of 3-dimethylaminopropiophenone to 3-(dimethylamino)-1-phenyl-propan-1-ol, a potential building block for the synthesis of the antidepressant agent fluoxetine, we investigated various reaction conditions for the hydrogenation of this base sensitive substrate.[11, 32-34] In line with previous reports, the hydrogenation proceeds under loss of the dimethylamino-group, using the procedure described before. We found that in a biphasic system, consisting of a substrate phase and KOH containing aqueous phase, 3-dimethylamino-propiophenone hydrochloride is readily hydrogenated (Scheme 5).



Scheme 5. Hydrogenation of 3-dimethylaminopropiophenone.

Furthermore, ketones like acetophenone are hydrogenated in excellent yields and with significantly higher turnover numbers than under neat conditions in this biphasic H_2O/substrate-system. Accordingly, acetophenone can be hydrogenated under these conditions using 0.01 mol% of pre-catalyst **3** with a yield of 98.8 % and a corresponding turnover number of 9880. The hydrogenation of cyclohexanone to cyclohexanol gives rise to slightly lower yields of 86.0 %. Overall, our method allows for the hydrogenation of ketones in a biphasic system, where the product can easily be isolated and no waste containing organic solvent is generated. As in green chemistry it is desirable to use water as solvent or co-solvent,[35-37] the described methods represents an environmentally benign and atom-economic transformation.

Conclusions

In conclusion, our investigations show that the nature of the heterocyclic donor group in PNX-type pincer ligands has a significant impact on the coordination chemistry and catalytic activity of the formed ruthenium(II) complexes. With weakening ruthenium - heteroatom bond to the heterocyclic donor, the catalytic activity of these ruthenium pre-catalysts in the acceptorless dehydrogenation of primary alcohols as well as the hydrogenation of ketones is diminished. Nevertheless we developed a method for the hydrogenation of simple ketones in biphasic water/substrate system under mild conditions using complexes **1** or **3** as pre-catalyst.

Acknowledgements

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Notes and references

‡ For experimental details, spectroscopic data, NMR spectra and details about the crystallographic data please see the supporting information.
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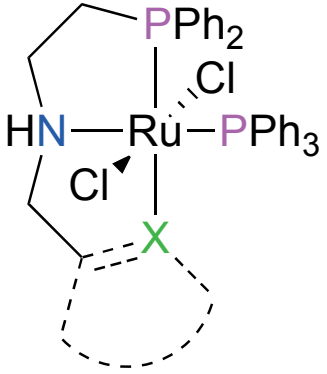

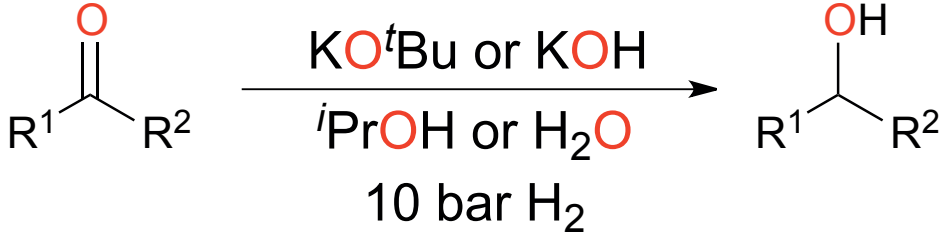

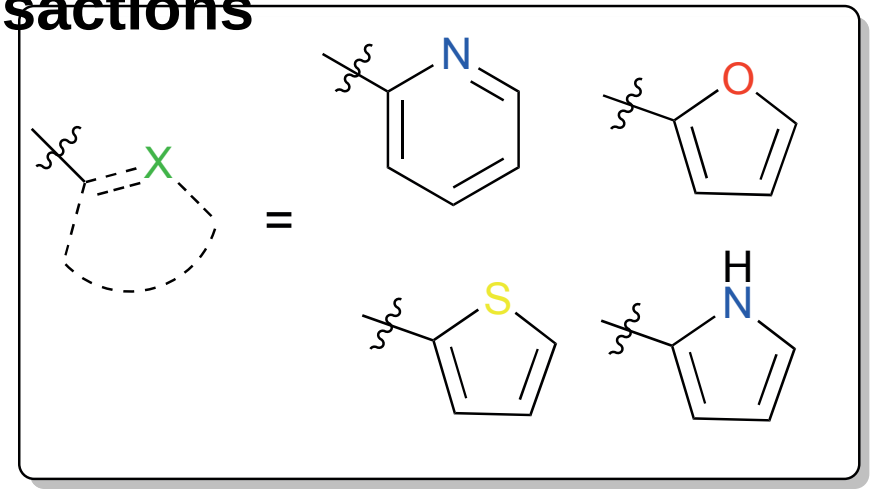

TOF up to 9990 h^{-1}