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Efficient Acceptorless Dehydrogenation of Secondary Alcohols to Ketones mediated by a PNN-Ru(II) Catalyst

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Abstract: Four types of ruthenium(II) complexes, [*fac*-PNN]RuH(PPh_3)(CO) (**A**), [*fac*-PN_HN]RuH(η^1-BH_4)(CO) (**B**), [*fac*-PN_HN]$RuCl_2$(PPh_3) (**C**) and [*fac*-PN_HN]RuH(η^1-BH_4)(PPh_3) (**D**) (where PN_HN and PNN are N-(2-(diphenylphosphino)ethyl)-5,6,7,8-tetrahydroquinoline-8-amine and its deprotonated derivative), have been synthesized and assessed as catalysts for the acceptorless dehydrogenation of secondary alcohols to afford ketones. It was found that **C**, in combination with *t*-BuOK, proved the most effective and versatile catalyst allowing aromatic-, aliphatic- and cycloalkyl-containing alcohols to be efficiently converted to their corresponding ketones with particularly high values of TON achievable. Furthermore, the mechanism for this PNN-Ru mediated process been proposed on the basis of a number of intermediates that have been characterized by EI-MS and NMR spectroscopy. These catalysts show great potential for applications in atom-economic synthesis as well as in the development of organic hydride-based hydrogen storage systems.

Introduction

The conversion of alcohols to carbonyl compounds can be regarded as one of the most important fundamental reactions in organic chemistry as evidenced by its extensive application in the synthesis of fine chemicals and pharmaceutical intermediates. Indeed, a raft of methods have been implemented over the years to accomplish this transformation.[1] Traditionally, stoichiometric amounts of common oxidants are used, but these reactants tend not only to be hazardous or toxic but can generate large quantities of noxious by-products.[2] In recent years, the development of transition-metal-catalyzed oxidation of alcohols using environmentally friendly oxidants such as O_2,[3] H_2O_2[4] or acetone[5] offers an improved approach. However, from the viewpoint of atom economy and reaction safety, the direct dehydrogenation of an alcohol to form a carbonyl compound (*e.g.*, a ketone or an aldehyde) without the need for an oxidant altogether, is an even more desirable and sustainable route as the only by-product is hydrogen.[6] The first reports of complexes that were capable of mediating this green transformation were reported by Robinson in the 1970s and Cole-Hamilton in the 1980's, in which well-defined ruthenium(II) complexes of the type [$Ru(OCOCF_3)_2(CO)(PPh_3)_2$][7] and [$RuH_2(N_2)(PPh_3)_3$][8] were employed. In the intervening years, the concept of acceptorless alcohol dehydrogenation (AAD)[9] has rapidly grown in interest with not only ruthenium[11] but iridium[10] catalysts now capable of the promoting the reaction. While both heterogeneous[12] and homogeneous[6,10,11] processes have been developed, the catalytic efficiency of the homogeneous variant remains insufficiently high to merit its industrial application and hence needs to be improved. For example, the ruthenium- and iridium-based homogeneous catalysts reported so far tend to require relatively high catalyst loadings in the 0.1 – 5 mol% range to achieve satisfactory conversions. Nevertheless, recent developments using pincer complexes that can operate using metal–ligand cooperation (MLC) show great potential for improving these catalytic performances. [3e,13,14,15]

In our previous work we have shown the ruthenium-hydride [*fac*-PNN]RuH(PPh_3)(CO) (PNN = 8-(2-diphenylphosphinoethyl)amido-trihydroquinoline) (**A**) (Chart 1) to be an effective catalyst in the coupling cyclizations of γ-amino alcohols with secondary alcohols to give pyridine or quinoline derivatives. Indeed, this system has proved highly efficient and amenable to catalyst loadings of as low as 0.025 mol% to achieve satisfactory results in this multistep dehydrogenative pathway.[16] Furthermore, **A** and its derivative [*fac*-PN_HN]RuH(η^1-BH_4)(CO) (**B**) (PN_HN = 8-(2-diphenylphosphinoethyl)-aminootrihydroquinoline) (Chart 1) can also be applied to the catalytic hydrogenation of esters. Notably, when combined with 5 mol% of $NaBH_4$, **A** or **B** can deliver high efficiencies for the hydrogenation of a wide range of esters under mild reaction conditions.[17]

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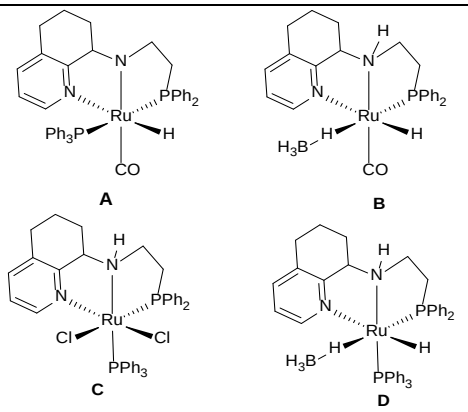
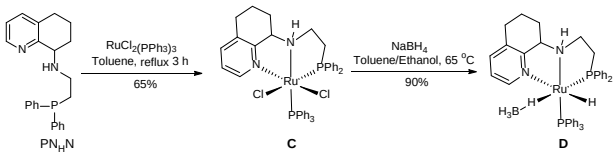


Chart 1. PNN-ruthenium(II) complexes (**A** – **D**) to be explored for the AAD reactions

Herein we explore the use of **A** and **B**, along with two new examples of this class of ruthenium(II) complex, [*fac*-PN_HN]$RuCl_2(PPh_3)$ (**C**) and [*fac*-PN_HN]$RuH(\eta^1\text{-}BH_4)(PPh_3)$ (**D**) (Chart 1), for the acceptorless dehydrogenation of alcohols. In particular, **C** is shown to exhibit unprecedented efficiency in the acceptorless dehydrogenation of secondary alcohols to afford the corresponding ketones, with very low catalytic loadings required to achieve high conversions. We view these complexes as showing great potential for applications in atom-economic synthesis and the development of organic hydride hydrogen storage systems. Furthermore, we propose a mechanism for the catalyzed acceptorless dehydrogenation reactions that is based on various intermediates that have been characterized by EI-MS and NMR spectroscopy.

Results and discussion

Synthesis and characterization of PNN-ruthenium complexes



Scheme 1. Synthesis of PNN-ruthenium complexes **C** and **D**

Reaction of $RuCl_2(PPh_3)_3$ with 8-(2-diphenylphosphinoethyl)-aminotrihydroquinoline (PN_HN)[16] in toluene at 100 ºC for 3 hours gave on work-up, [*fac*-PN_HN]$RuCl_2(PPh_3)$ (**C**), in good yield (Scheme 1). Complex **C** displays peaks in its ESI mass spectrum corresponding to a protonated molecular ion and a fragmentation peak attributable to a loss of chloride from the molecular ion. Unexpectedly, on standing in deuterated chloroform for four hours, **C** undergoes partial isomerization resulting in a mixture consisting of **C** and **C'** in a 72:28 ratio. The $^{31}P\{^1H\}$ NMR spectrum of **C** exhibits two mutually coupled doublets at δ 55.68 and δ 45.61 with a coupling constant of *ca.* 28 Hz corresponding to a *cis*-arrangement of the phosphine donors. In **C'** a *cis*-arrangement of the phosphine donors is again apparent with the two doublets (each *ca.* $^2J(PP)$ = 28 Hz) in this case appearing at δ 48.12 and δ 43.16 (see SI). Crystals of the major isomer **C** suitable for a single-crystal X-ray diffraction study could be grown by slow diffusion of *n*-hexane into its solution in dichloromethane. The structure consists of a distorted octahedral geometry at ruthenium with the PN_HN ligand adopting a *fac*-configuration with the triphenylphosphine molecule *trans* to the amine donor and the two chloride ligands mutually *cis* (Fig. 1, see SI). The borohydride derivative of **C**, [*fac*-PN_HN]$RuH(\eta^1\text{-}BH_4)(PPh_3)$ (**D**), could be readily obtained by reacting complex **C** with $NaBH_4$ in a toluene/ethanol mixture at 65 ºC; the structure of **D** was confirmed by multinuclear NMR spectroscopy, MS and elemental analysis (see SI).

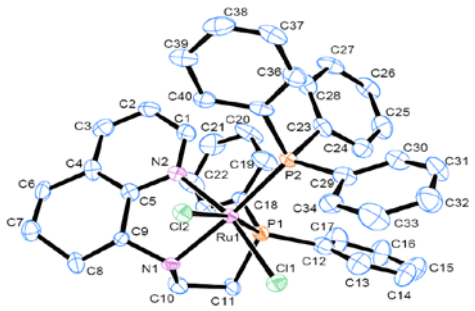
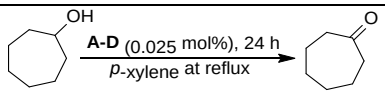


Fig. 1. ORTEP representation of **C**. All hydrogen atoms have been omitted for clarity. Bond lengths [Å] and angles [deg]: Ru(1)-N(2) 2.089(5), Ru(1)-N(1) 2.162(5), Ru(1)-P(1) 2.2622(17), Ru(1)-P(2) 2.3249(17), Ru(1)-Cl(1) 2.4275(17), Ru(1)-Cl(2) 2.5013(16), P(1)-Ru(1)-Cl(2) 167.48(6), P(2)-Ru(1)-Cl(2) 89.40(6), Cl(1)-Ru(1)-Cl(2) 84.44(6), N(2)-Ru(1)-N(1) 78.61(19), N(2)-Ru(1)-P(1) 90.62(14), N(1)-Ru(1)-P(1) 84.06(14).

Catalytic Studies

Firstly, we screened the catalytic activity of all four PNN-ruthenium complexes, **A** – **D**, for the test AAD reaction of cycloheptanol to give cycloheptanone; the results are listed in Table 1.

Table 1. Acceptorless dehydrogenation of cycloheptanol by complexes **A** - **D**.[a]



Entry	Cat.	Base	Conv. (%)[b]
1	**A**	*t*-BuOK	50
2	**B**	none	26
3	**B**	*t*-BuOK	52
4	**C**	*t*-BuOK	76
5	**D**	none	35
6	**D**	*t*-BuOK	74
7	1[c]	*t*-BuOK	12
8	2[d]	*t*-BuOK	16

[a] Reaction conditions: cycloheptanol (5 mmol), **A** - **D** (1.25×10^{-3} mmol), *t*-BuOK (5 mmol) in *p*-xylene (5 mL) at 160 ºC (oil bath temperature) for 24 hours.
[b] The conversion was determined by GC analysis using dodecane as an internal standard .
[c] 1 is $RuH(CO)(PPh_3)_3$ (1.25×10^{-3} mmol) as catalyst.
[d] 2 is $RuCl_2(PPh_3)_3$ (1.25×10^{-3} mmol) as catalyst.

Typically, the catalytic screen was performed using an equimolar ratio of cycloheptanol to the *t*-BuOK base (5 mmol), using 0.025 mol% of the corresponding ruthenium complex in *p*-xylene at reflux for 24 hours. To our delight, all the ruthenium species were active with the conversion to cycloheptanone being 50% for **A**, 52% for **B**, 76% for **C** and 74% for **D** (Table 1, entries 1, 3, 4 and 6). In the absence of *t*-BuOK, the conversion dropped to 35% using **D**, while for **B** it lowered to 26% (Table 1, entries 2 and 5). In order to rule out any catalyst precursor effects on performance, $RuH(CO)(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ in the presence of 5 mmol *t*-BuOK, were independently evaluated under the same conditions; the conversion to cycloheptanone in these cases was 12 and 16%, respectively (Table 1, entries 7, 8). Overall, the best results were obtained using the PNN-ruthenium(II) complexes **C** and **D**. However, due to **D** being synthesized from **C,** coupled with the fact that **D** showed some instablity in solution, we choose **C** as our catalyst for subsequent studies.

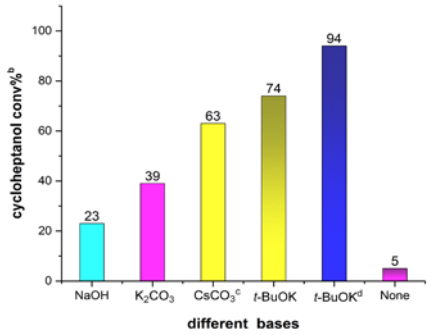


Fig. 2 The acceptorless dehydrogenation of cycloheptanol by complex **C** under different bases[a]

[a] Reaction conditions: cycloheptanol (5 mmol), base (5 mmol), **C** (1.25×10^{-3} mmol) in toluene (5 mL) at 130 °C (oil-bath temperature) for 24 hours.

[b] The conversion was determined by GC using dodecane as an internal standard.

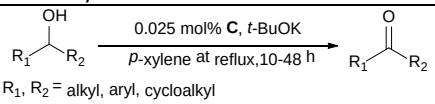
[c] Base: $CsCO_3$ (2.5 mmol).

[d] Reaction conditions: cycloheptanol (5 mmol), *t*-BuOK (5 mmol), **C** (1.25 µmol), at 160 ºC (oil-bath temperature) in *p*-xylene (5 mL) in 36 hours.

Secondly, with a view to establishing the most compatible base, the acceptorless dehydrogenation of cycloheptanol to cycloheptanone with **C** as catalyst was screened with four different types of bases, NaOH, K_2CO_3, $CsCO_3$ and *t*-BuOK (Fig. 2, see SI, Table S1), in toluene at reflux. It was found that the type of base introduced had a significant effect on the conversion of cycloheptanol to cycloheptanone with *t*-BuOK the standout performer. When equivalent molar ratios of NaOH or K_2CO_3 were employed (5 mmol), the conversion observed after 24 hours is markedly less (23 and 39%, respectively) than that seen with *t*-BuOK (74%). With 2.5 mmol of $CsCO_3$ (relatively expensive and toxic), 69% of cycloheptanone was produced after 24 hours. On increasing the temperature to reflux in *p*-xylene, the conversion using **C**/*t*-BuOK increased to 76% in 24 hours and 94% in 36 hours (see SI, Table S1). Notably in the absence of base and under the same reaction conditions using **C** as catalyst, only 5% of cycloheptanone was produced after 24 hours. Overall, carrying out the AAD in *p*-xylene at reflux using *t*-BuOK as the base proved the optimal operating conditions to deliver high conversions to cycloheptanone.

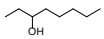
To explore the versatility of **C**, a broad range of secondary alcohols were selected for study in the AAD using the optimal conditions established (*viz*., alcohol: *t*-BuOK = 1:1, 0.025 mol% **C** in *p*-xylene at reflux); the results are compiled in Table 2.

Table 2. Substrate scope in the acceptorless alcohol dehydrogenation by **C**.[a]



R_1, R_2 = alkyl, aryl, cycloalkyl

Entry	Alcohol	Product	t (h)	Conv. (%)[b]	TON
1			24	23	920
2			24	43	1720
3			24 36	76 94	3040 3760
4			24	100	4000
5			24	100	4000
6			24	98	3920
7			24	100	4000
8			24	91	3640
9			24	100	4000
10			24	97	3880
11			24	96	3840
12			24	90	3600
13			24	94	3760
14			24	95	3800
15			24	68	2720
16			10	97	3880
17			24	27	1080
18			24	30	1200
19			24	21	840

20			10	100	4000
21[c]			40	100	8000
22			48	29	1160
23			48	27	1080
24[d]			48	41	1640
25			24	55	2200
			24[e]	78	780

[a] Reaction conditions: alcohol (5 mmol), **C** (1.25×10^{-3} mmol) and *t*-BuOK (5 mmol) in *p*-xylene (5 mL) at 160 °C (oil bath temperature).

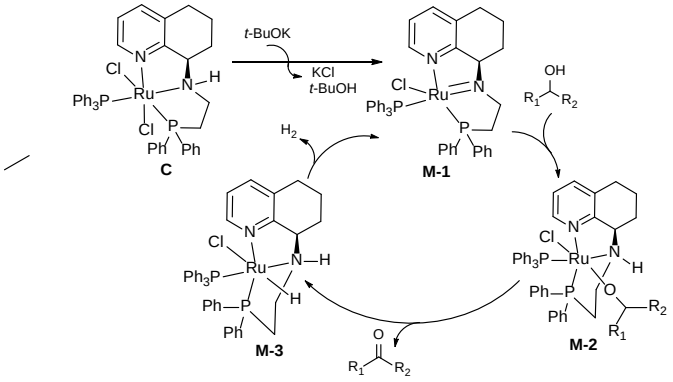
[b] The conversion was determined by GC using dodecane as an internal standard.

[c] Under the same reaction conditions but with **C** (0.625×10^{-3} mmol).

[d] The reaction temperature at 50 °C.

[e] Reaction conditions: Benzyl alcohol (10 mmol), **C** (0.1 mmol) and t-BuOK (1 mmol) in toluene (5 mL) at 117 ºC (oil-bath temperature).

It was found that for the cyclic alcohols, the smaller ring sizes (n ≤ 6) led to very low conversions, *e.g.*, only 23% and 34% of cyclohexanone and cyclopentanone were obtained after 24 hours, respectively (Table 2, entries 1-2). By contrast, the larger cyclic alcohols (n ≥ 7) gave excellent conversions to the corresponding ketones, with cycloheptanone and cyclooctanone being obtained in 94% in 36 hours and 100% in 24 hours, respectively (entries 3-4). With regard to the aromatic-containing secondary alcohols, the conversions to the corresponding ketones were usually high, for example 1-phenylethanol, diphenylmethanol, 4-methylphenyl-(phenyl)methanol, 1,2,3,4-tetrahydro-1-naphthalenol, 1-indanol and 10, 11-dihydro-5*H*-dibenzo [*a*, *d*] cyclohepten-5-ol, were amenable to 100%, 98%, 100%, 91%, 100% and 97% conversions in 24 hours, respectively (Table 2, entries 5-10). With regard to secondary alcohols with electron-rich groups (Me or MeO) in the aromatic ring, they also gave very high conversions (Table 2, entries 11-13). Even the aromatic-containing secondary alcohols with sterically hindered groups gave moderate to high conversions (Table 2, entries 14-15). Conjugative and electronic-rich effects due to the presence of the aromatic ring are likely responsible for this good performance. On the other hand, the alcohols containing electron-withdrawing groups in the aromatic ring gave very poor conversions: percentage conversions for 4-chlorophenyl(phenyl)-methanol, 1-(4-fluorophenyl)-ethanol, 1-(2-fluorophenyl)ethan-1-ol being only 27%, 30% and 21% (Table 2, entries 17-19). These findings imply that catalyst **C** is very sensitive to the structure of the secondary alcohol employed. Alkyl-containing alcohols can also be effectively dehydrogenated particularly those incorporating a C=C double bond (Table 2, entries 16, 20), *e.g.*, 1-octen-3-ol could be quantitatively converted to 1-octen-3-one in only 10 hours (Table 2, entry 20). Even when the catalyst loading was reduced to 0.0125 mol%, 100% conversion of 1-octen-3-ol could be achieved in 40 hours leading to a remarkable TON of 8000 (100% conversion) (Table 2, entry 21). For alkyl-containing alcohols without an alkene unit in the chain such as nonan-3-ol and nonan-2-ol, the conversions were lower at 29% and 27% in 48 hours, again highlighting the importance of conjugative effects in the transformation (Table 2, entries 22 and 23). As for benzyl alcohol as the primary alcohol, the conversion to benzaldehyde was lower at 41% after 48 hours at a relatively low temperature (50 °C) (Table 2, entry 24). However, at higher temperatures (>117 °C), benzyl benzoate was produced instead of the corresponding benzaldehyde (Table 2, entry 25). A few other examples of primary alcohols were also converted using **C** to the corresponding esters (see SI, Table S2). These findings are consistent with the work reported by Gusev.[18]

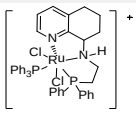
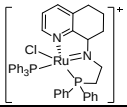


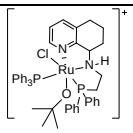
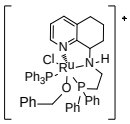
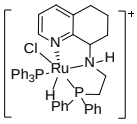
Scheme 2. Proposed mechanism for the acceptorless dehydrogenation of secondary alcohols catalyzed by **C**

Mechanistic and Characterization aspects

A proposed catalytic cycle for these AAD reactions that makes use of bifunctional metal-ligand cooperativity,[13j,k,19] is shown in Scheme 2. Firstly, **C** undergoes the loss of H^+ and Cl^-, under the action of the strong base *t*-BuOK, forming amide **M-1** along with KCl and *t*-BuOH. Crabtree has previously noted that the NH of a pincer ligand needs to be deprotonated to form the active catalyst and we similarly propose a related step occurring during the conversion of **C** to **M-1**.[6] Subsequently, the hydroxyl group in the secondary alcohol adds across the Ru=N bond in **M-1**, to form intermediate **M-2**. The C*H*R_1R_2O hydrogen atom belonging to the coordinated alkoxide in **M-2** transfers to the Ru center to generate hydride **M-3** and ketone. In the last step elimination of hydrogen gas from **M-3** occurs reforming **M-1**.

Table 3. Species detected using ESI mass spectrometry under catalytic conditions using catalyst **C**

Intermediate	ESI MS: detected species	*m/z*	Structural assignment
C	[**C**+1]$^+$	795.4	
M-1	[(**M-1**)+1]$^+$	759.1	

M-2	[(**M-2**)+1]$^+$	831.8	
M-2"	[(**M-2"**)+1]	867.8	
M-3	[(**M-3**)+1]$^+$ [(**M-3**)+Na]$^+$	761.3 783.9	

In order shed some light on this mechanism, we monitored the reaction of an equimolar ratio of **C**, *t*-BuOK and benzyl alcohol in $CDCl_3$ at 45 ºC for 24 hours, by ESI-MS and ^{1}H NMR spectroscopy. In the ESI-MS peaks corresponding to **C** along with four different intermediates have been identified: **M-1** [(PNN)RuCl(PPh_3)], **M-2** [(PN_HN)RuCl(O-*t*-Bu)(PPh_3)], **M-2"** [(PN_HN)RuCl(OCH_2Ph)(PPh_3)] and **M-3** [(PN_HN)RuCl(H)(PPh_3)] (Table 3 and SI).[18a] At the same time, the ^{1}H NMR spectrum was recorded after 1, 6 and 24 hours (see Fig. 3). Close examination of the spectra reveals the signal corresponding to the benzyl alcohol CH_2 group at 4.72 ppm decreases in intensity with the time: at t = 0 h, peak area = 3.76; at t = 1 h, peak area = 3.57; at t = 6 h, peak area = 3.49; at t = 24 h, peak area = 3.14. Furthermore, after one hour a new peak at 5.32 ppm forms with a peak area of 0.25 which can be assigned to the benzyl alkoxide intermediate **M-2''**. After 6 hours, this peak area increases in intensity to 0.35 while a new peak at 10.5 ppm becomes visible which can be attributed to the formation of benzaldehyde. After 24 hours, the peak area at 5.32 ppm for **M-2"** integrates to 0.31 which is similar in intensity to that observed after 6 hours. This would therefore suggest that an equilibrium is established between **M-2"** and benzyl alcohol. In summary, all this *in-situ* determined data firmly support the steps shown in the catalytic cycle in Scheme 2.

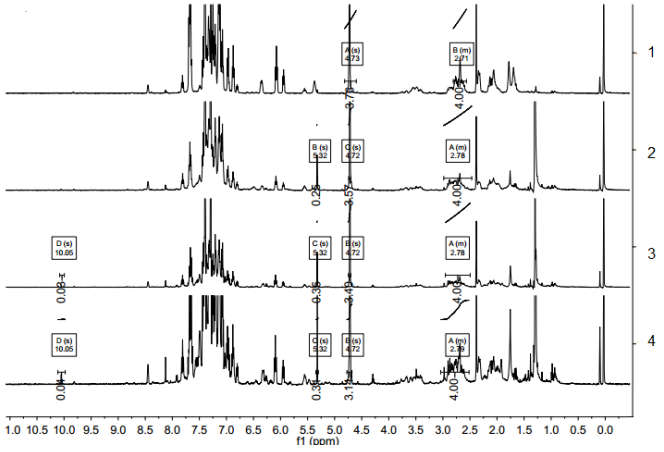


Fig. 3. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of an equimolar ratio of **C** and benzyl alcohol recorded: 1. after sample dissolution, 2. with *t*-BuOK (1 eq.) at 45 ºC after 1 hour, 3. with *t*-BuOK (1 eq.) at 45 ºC after 6 hours, 4. with *t*-BuOK (1 eq.) at 45 ºC after 24 hours.

Conclusions

Four types of PNN-Ru(II) complexes, **A** – **D**, have been evaluated as catalysts in the acceptorless dehydrogenation of secondary alcohols to give ketones. Complex [*fac*-PN_HN]$RuCl_2(PPh_3)$ (**C**), in the presence of *t*-BuOK, proved the most suitable and was able to operate efficiently with a catalyst loading of just 0.025 mol%. Indeed, using **C**/*t*-BuOK as catalyst, seventeen different kinds of secondary alcohols could be dehydrogenated to give their corresponding ketones with yields in the range 21-100%; structural variations in the substrate greatly affect the catalyst performance. In addition, a mechanism for the PNN-Ru mediated dehydrogenation has been proposed that is supported by various intermediates that have been characterized by EI-MS and NMR spectroscopy.

Experimental section

General information.

All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of nitrogen. All solvents were reagent grade or better and were used after being distilled under nitrogen. Most of the chemicals used in the catalytic reactions were re-purified according to standard procedures (*e.g.*, vacuum distillation). All ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{31}P NMR spectra were recorded on a Bruker AV-III (500 MHz) spectrometer. GC analyses were carried out on an Agilent 6820 instrument using an OV-1701 column. GC conditions: Injector Temp: 250 ºC; Detector Temp: 250 ºC; column temperature 150 ºC. ESI-MS analysis was performed on a 3200 QTRAP 1200 infinity series instrument using a column C18, acetonitrile: water = 70:30, flow rate = 1 mL / min, electronic energy = 50 eV, Q1MS scan range = 100~1000.

Synthesis of complex C

$RuCl_2(PPh_3)_3$ (2.00 g, 2.087 mmol) and N-(2-(diphenylphosphino)-ethyl)5,6,7,8-tetrahydro-quinolin-8-amine (0.75 g, 2.087 mmol) were dissolved in toluene (100 mL) and stirred at 100 ºC for 3 h. After being cooled to room temperature, the resulting precipitate was filtered and washed with diethyl ether (3 × 10 mL). The title complex was obtained as pale yellow solid (1.08 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (q, *J* = 7.8, 7.2 Hz, 6H), 7.43 (t, *J* = 8.7 Hz, 2H), 7.39 – 7.18 (m, 10H), 7.17-7.06 (m, 8H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 5.35 (s, H, N-H), 3.54 (q, *J* = 48.6, 38.2 Hz, 1H), 2.86 – 2.57 (m, 4H), 2.39 – 2.29 (m, 2H), 2.17-1.98 (m, 3H), 1.78 – 1.62 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.21, 154.69, 138.71, 137.89, 137.17, 136.87, 136.77, 135.23, 135.18, 135.10, 135.07, 135.02, 134.90, 134.78, 134.71, 134.00, 133.93, 133.57, 131.42, 131.35, 129.07, 128.84, 128.78, 128.62, 128.26, 127.83, 127.76, 127.61, 127.54, 127.34, 127.29, 127.27, 127.21, 127.14, 127.08, 127.01, 125.34, 122.59, 61.22, 45.65, 44.78, 37.98 (d, *J* = 27.2 Hz), 28.96, 27.97, 21.50, 20.73 (CH_3-Toluene)

^{31}P NMR (202 MHz, $CDCl_3$) δ 55.68 (d, *J* = 27.6 Hz), 45.61 (d, *J* = 27.8 Hz).ESI-MS (m/z) Calcd for [$C_{41}H_{41}Cl_2N_2RuP_2$], 795.1; found: 795.4 [**C**+1]$^+$; Calcd for[$C_{41}H_{40}Cl_2N_2RuP_2$], 759.1; found: 759.6 [**C**-Cl]$^+$.

Anal. Calcd for $C_{41}H_{40}Cl_2N_2RuP_2$: C, 61.96; H, 5.073; N, 3.52. Found: C, 61.77; H, 5,159; N, 3.34.

On standing in $CDCl_3$ for 4 h, complex **C** was obtained as a mixture of two isomers, **C**/**C'** 72:28. No free PPh_3 was detected after this

time (NMR sample: 20 mg of **C** in 0.8 mL $CDCl_3$).

C and **C'**

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.74 (**C'**), 161.21 (**C**), 157.58 (**C'**), 154.69 (**C**), 138.71, 137.89, 137.17, 136.87, 136.77, 135.23, 135.18, 135.10, 135.07, 135.02, 134.90, 134.78, 134.71, 134.00, 133.93, 133.57, 131.42, 131.35, 129.07, 128.84, 128.78, 128.62, 128.26, 127.83, 127.76, 127.61, 127.54, 127.34, 127.29, 127.27, 127.21, 127.14, 127.08, 127.01, 125.34, 122.59 (**C**), 120.98 (**C'**), 61.93 (**C'**), 61.22 (**C**), 45.65 (**C**), 44.78 (**C'**), 37.98 (d, *J* = 27.2 Hz, **C**), 35.11 (d, *J* = 27.6 Hz, **C'**), 28.96 (**C**), 28.27 (**C'**) 27.97 (**C**), 27.21 (**C'**), 21.50 (**C**), 21.21 (**C'**), 20.73 (CH_3-Toluene).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) **C**: δ 55.68 (d, *J* = 27.6 Hz), 45.61 (d, *J* = 27.8 Hz); **C'**: δ 48.12 (d, *J* = 27.7 Hz), 43.16 (d, *J* = 29.3 Hz).

Catalytic study details.

Under an atmosphere of argon, a Schlenk vessel equipped with a stir bar, was loaded with the ruthenium complex (**A** - **D**) (1.25×10^{-3} mmol) to be investigated, the corresponding alcohol (5 mmol) and the desired amount of base (NaOH, K_2CO_3, $CsCO_3$, *t*-BuOK) (1 - 5 mmol) in *p*-xylene (5 mL) (or toluene). The reaction was then stirred and heated to the desired oil-bath temperature (130 °C or 160 °C) with the reaction vessel open to the bubbler. After the specified reaction time (10 - 48 h), the resultant solution was cooled to room temperature and the reaction mixture filtered through a plug of silica gel and then analyzed by GC using dodecane as an internal standard,[11c,e] employing an OV-1701 column column on Agilent 6820 instrument.

X-ray Structure Determination

A single-crystal X-ray diffraction study of **C** was conducted on a Rigaku Sealed Tube CCD (Saturn 724+) diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 173(2) K. Cell parameters were obtained by global refinement of the positions of all collected reflections (see Table S3 in SI). Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed in calculated positions. Using the SHELXL-97 package, structural solution and refinement were performed.[20]

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Journal Name

ARTICLE

Graphical for Table of Contents

Efficient Acceptorless Dehydrogenation of Secondary Alcohols to Ketones mediated by a PNN-Ru(II) Catalyst

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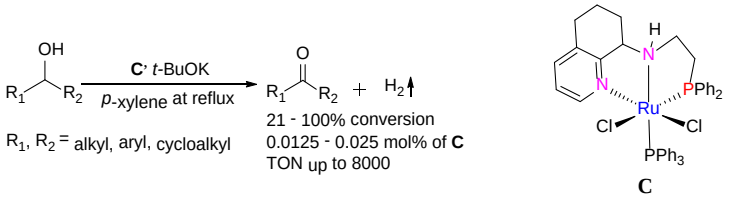

The ruthenium(II) complex, [*fac*-PN_HN]$RuCl_2(PPh_3)$ (**C**), in combination with *t*-BuOK proved an effective and versatile catalyst allowing aromatic-, aliphatic- and cycloalkyl-containing alcohols to be efficiently converted to their corresponding ketones with particularly high values of TON achievable.