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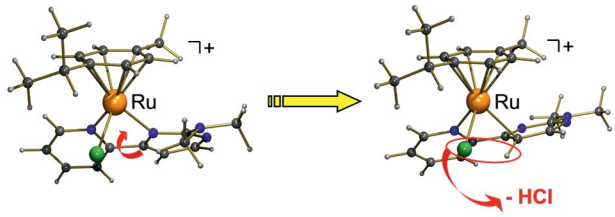
C–H Activation

Keywords: Transfer hydrogenation / Ruthenium / C–H activation / Mass spectrometry / Density functional calculations



Phosphane-free air-stable ruthenium complexes catalyze the transfer hydrogenation of acetophenone in the absence of a base. Intramolecular C–H bond cleavage gives rise to a new catalyst activation mechanism, which was investigated through isotopic labelling, mass spectrometry and quantum chemical calculations.

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C–H Activation at a Ruthenium(II) Complex – The Key Step for a Base-Free Catalytic Transfer Hydrogenation?

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Dedicated to Prof. Dr. Werner Uhl on the occasion of his 60th birthday

Keywords: Transfer hydrogenation / Ruthenium / C–H activation / Mass spectrometry / Density functional calculations

Ruthenium(II) complexes [(η^6-cymene)RuCl(apypm)]BPh_4 with bidentate 2-amino-4-(2-pyridinyl)pyrimidine (apypm) ligands catalyze the transfer hydrogenation of acetophenone. Their activities are strongly dependent on the substituent pattern of the pyrimidine ring. Complexes bearing a primary amino group in the 2-position of the pyrimidine ring do not perform the catalysis in terms of a "bifunctional mechanism", although they possess protic hydrogen atoms at the amino moiety in close proximity to the metal site. Systems containing tertiary dialkylated amino substituents at the apypm ligand are the first examples of air-stable and phosphane-free transfer-hydrogenation catalysts that show high activities even in the absence of a base. A new mechanism for the catalyst activation in the absence of an external base is proposed on the basis of ESI-MS investigations and ab initio calculations combined with isotope labelling: C–H bond cleavage at the pyrimidine ring is the crucial step for the generation of the catalytically active species.

Introduction

The catalytic transfer hydrogenation of ketones provides access to a wide range of alcohols, including chiral ones, which are important in pharmaceutical, agrochemical, flavour, fragrance, materials and fine chemical synthesis.[1] Under basic conditions and mainly with *i*PrOH as the solvent, ruthenium(II) complexes are the most active systems. Thus, a broad variety of ruthenium compounds bearing arene, PP, NN, NO, or NPN ligands have been investigated for transfer-hydrogenation reactions.[2] Noyori et al. developed a series of ruthenium(II) arene complexes equipped with chiral N,N ligands. These compounds are highly active and stereoselective in the asymmetric hydrogenation of ketones and imines in the presence of a base.[3] Both the activity and the selectivity can even be improved by the presence of an N–H functionality in the ligand in close proximity to the metal site. This finding was explained as a cooperation between the metal site and the ligand and was denominated as "bifunctional catalysis".[4] In succession, others have developed ligands for the bifunctional ruthenium-catalyzed hydrogenation and transfer hydrogenation containing amino alcohol,[5] aminoamide,[6] and aminocarboxylate[7] moieties with at least one hydrogen atom bound to a nitrogen atom. The formation of metal hydrido intermediates was generally proposed to be part of the hydrogenation mechanism.[8]

In 2005, Baratta et al. developed arene-free ruthenium catalysts that are extremely active in the transfer hydrogenation of acetophenone with NaOH as the base.[9] From a mechanistic point of view, the main difference between the Baratta and Noyori systems is that, in the former one, the alcohol and the ketone coordinate to the metal centre during the catalytic process (so-called "inner-sphere" mechanism), whereas in Noyori's system, the substrate does not coordinate to the metal site but interacts with the ligands (so-called "outer-sphere mechanism").[10]

In most cases, a base such as NaOH, KOH or KO*t*Bu is required to generate the active and air-sensitive metal hydrido species.[1d–1f,8,11] However, there are some studies in which no base was added and in which air-sensitive hydridoruthenium complexes were introduced directly.[10,12]

During the past years, we have been working on the development of new N-heterocyclic ligands for homogeneous catalysis mainly containing pyrazolyl and pyrimidinyl units.[13] As these groups can easily be functionalized with electron-donating and -withdrawing functions without changes to the steric properties of the ligand, they are espe-

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cially advantageous for the elucidation of structure–reactivity relationships in catalysis based on the electronic impact of the ligand.[14] Furthermore, it is simple to graft these ligands onto inorganic supports, as the N–H functions enable the generation of efficient linkers in just a few steps.[15] Here, we present a study on the application of a series of pyridinylpyrimidines for ruthenium(II)-catalyzed transfer hydrogenation with a special focus on the relationship between ligand structure and catalytic activity.

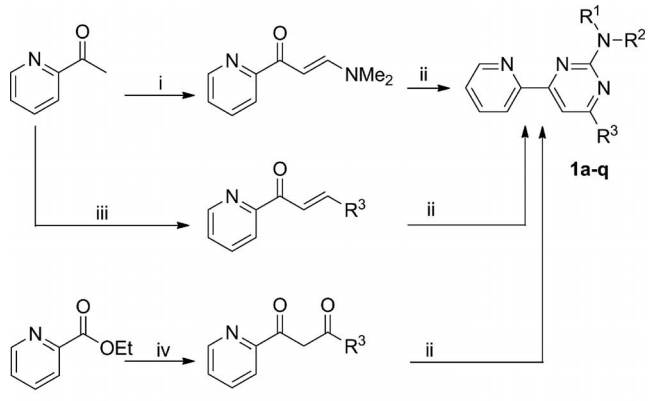
Results and Discussion

Ligand and Complex Syntheses

2,2-Bipyridyl is probably the most frequently used aromatic *N*,*N*-chelating ligand in coordination chemistry.[16] However, pyridine chemistry makes it difficult to efficiently introduce a broad variety of substituents into the ligand. As we were looking for N,N′-donors bearing an amino group in close proximity to the coordinating nitrogen atom in combination with other functional groups to elucidate the influence of these groups on the bifunctional catalytic transfer hydrogenation, we switched to the 2-amino-4-(2-pyridinyl)pyrimidine motif. The chemistry of pyrimidine and its derivatives is well established,[17] and 2-amino-4-(2-pyridinyl)pyrimidines can be obtained in straightforward syntheses starting from versatile 2-acetylpyridine or pyridine-2-carboxylic acid ester (Scheme 1).[18]

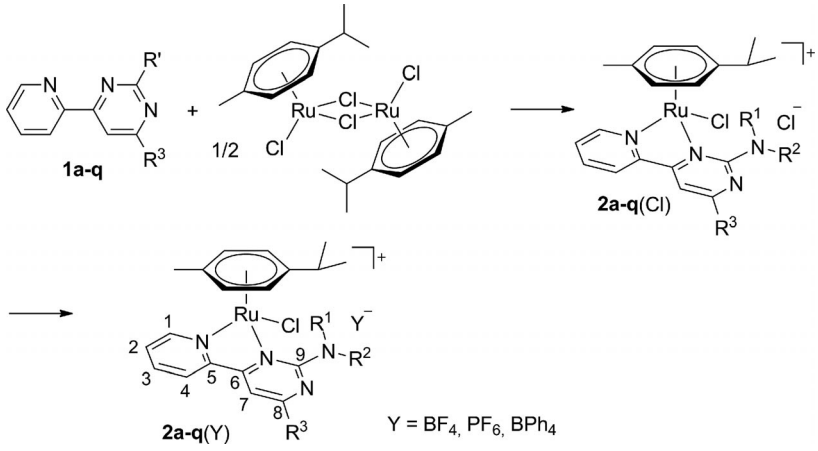
The reaction of the intermediates shown in Scheme 1 with guanidinium salts in the presence of a base gave the desired ligands **1a**–**1q** in good yields. Three members of the 2-amino-4-(2-pyridinyl)pyrimidine series (**1m**, **1p** and **1q**) were characterized structurally by single-crystal X-ray diffraction (see Supporting Information).

The treatment of **1a**–**1q** with the ruthenium(II) precursor $[(\eta^6\text{-cymene})Ru(Cl)(\mu^2\text{-}Cl)]_2$ at room temperature in dichloromethane gave the red-brown cationic ruthenium(II) complexes $[(\eta^6\text{-cymene})Ru(Cl)(apypm)]Cl$ [**2a**–**2q**(Cl); apypm = chelating 2-amino-4-(2-pyridinyl)pyrimidine ligand] in almost quantitative yields (Scheme 2). For catalyst optimization, the chloride anion was exchanged with three larger and, thus, more weakly coordinating anions (BF_4^-, PF_6^-, BPh_4^-), which additionally enforced the crystallization of the compounds. Thus, the ruthenium(II) complexes **2a**–**2q**(Y) were obtained directly when freshly pre-



1	R^1	R^2	R^3
a	H	H	H
b	H	^{n}Pr	H
c	H	^{n}Bu	H
d	H	^{n}Oct	H
e	H	^{i}Pr	H
f	H	(*S*)-HN(CH)(CH$_3$)(C$_6$H$_5$)	H
g	H	(*R*)-HN(CH)(CH$_3$)(C$_6$H$_5$)	H
h	Me	Me	H
i		$(CH_2)_4$	H
j		$(CH_2)_5$	H
k	H	H	C_6H_5
l	H	H	1-naphthyl
m	H	H	C_6H_4OMe
n	H	H	$C_6H_4O^nBu$
o		$(CH_2)_4$	C_6H_4OMe
p	H	H	^{t}Bu
q	Me	Me	^{t}Bu

Scheme 1. (i) $HC(NMe_2)(OMe)_2$, 4 h, reflux; (ii) $[C(NH_2)_3]_2(CO_3)$ then $[(R^1R^2N)C(NH_2)_2]_2(SO_4)$, EtOH, reflux, 24 h; (iii) propanol, $NH(Et)_2$, arylaldehyde, 12 h, reflux; (iv) tetrahydrofuran (THF), NaH, *t*BuC(O)Me, 12 h, reflux.



Scheme 2. Synthesis of the ruthenium(II) complexes; the numbering of the compounds is according to the Table provided in Scheme 1.

pared complexes **2a**–**2q**(Cl) were stirred with $NaBPh_4$, $NaBF_4$ or KPF_6.

Owing to the two different N-donor moieties, the metal site becomes a centre of chirality, which leads to two diastereotopic methyl groups and four magnetically inequivalent aromatic C–H sites at the cymene ligand. This is clearly demonstrated by the ^1H and ^{13}C NMR spectra of the ruthenium complexes. The methyl groups of the isopropyl units appear as two doublets at $\delta \approx 0.8$ and 0.9 ppm in the ^1H NMR spectra, and four peaks at $\delta = 82$–86 ppm in the ^{13}C NMR spectra can be assigned to four magnetically inequivalent tertiary aromatic C atoms of the cymene ring. The coordination of the 2-amino-4-(2-pyridinyl)pyrimidines to the Lewis acidic ruthenium(II) centre causes a shift of the 1-H resonance to lower field (for the numbering see Scheme 2): $\delta \approx 9.50$ ppm for ligands with R = NH_2, $\delta \approx 9.48$ ppm for ligands with R = NHAlkyl, $\delta \approx 9.32$ ppm for R = NMe_2 and $\delta \approx 9.24$ ppm for R = $N(CH_2)_4$. This is quite a pronounced influence for a substituent located at the other side of the ligand and is an indirect hint to the electronic situation at the ruthenium(II) centre, which should become more electron rich in the series R = NH_2 < NHAlkyl < NMe_2 < $N(CH_2)_4$. The resonances of the protons 2-H ($\delta \approx 7.83$ ppm) and 3-H ($\delta \approx 8.24$ ppm) are almost independent from the pyrimidine ring substituents, and 4-H shows a similar but less pronounced behaviour to 1-H. The 7-H proton of the pyimidine moiety is sensitive to the presence ($\delta \approx 8.21$–8.39 ppm) or absence ($\delta \approx 7.69$–7.86 ppm) of aromatic substituents at the 8-positition, and the chemical shift of 8-H is almost independent from the amine substituent.

In the ^{13}C NMR spectra, nine carbon resonances for the nine carbon atoms of the cymene ligand can be assigned, which proves that the molecule has a chiral centre. Generally, the ^{13}C NMR shifts are less sensitive towards the substitution pattern of the 2-amino-4-(2-pyridinyl)pyrimidine ligands than the ^1H NMR shifts. Solely, C-7 of complex **2l**(BPh_4) is shifted by ca. 10 ppm towards lower field with respect to the other compounds. This is probably because of the deshielding effect of the naphthyl substituent. The chiral pyrimidinylpyridines **1f** and **1g** lead to 1:1 mixtures of diastereomeric cymene ruthenium(II) cations.

Solid-State Structures

Single crystals suitable for X-ray diffraction studies were obtained for the ruthenium(II) complexes **2a**(PF_6), **2k**(BPh_4), **2p**(BPh_4), **2b**(BPh_4), **2h**(BPh_4), **2i**(BPh_4),

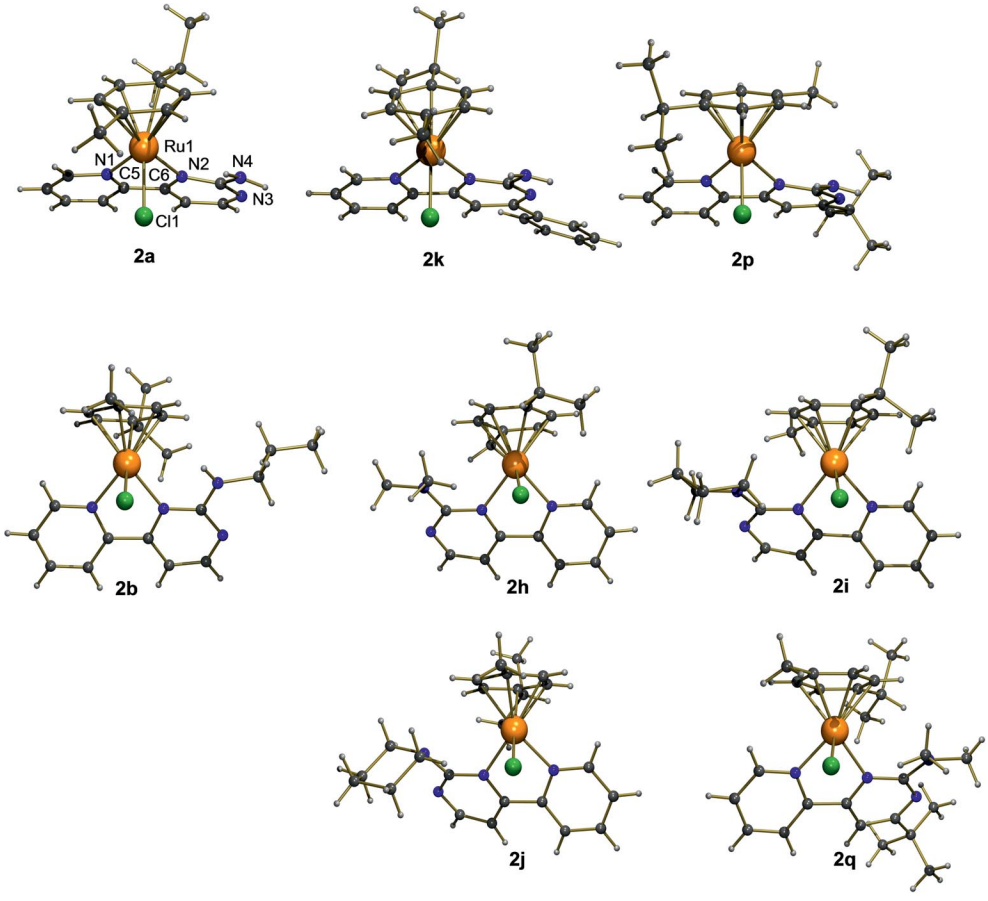


Figure 1. Molecular structures of the cations **2a**$^+$, **2k**$^+$, **2p**$^+$ (primary amino unit), **2b**$^+$ (secondary amino unit), **2h**$^+$, **2i**$^+$, **2j**$^+$ and **2q**$^+$ (tertiary amino unit) in the solid state. The counterions and cocrystallized solvent molecules are omitted for clarity. The atom numbering is identical to that for **2a**$^+$ for all structures.

Table 1. Characteristic bond lengths [Å], bond angles and torsion angles [°] for **2a**(PF_6), **2k**(BPh_4), **2p**(BPh_4), **2b**(BPh_4), **2h**(BPh_4), **2i**(BPh_4), **2j**(BPh_4) and **2q**(BPh_4).

	2a(PF_6)	**2k**(BPh_4)	**2p**(BPh_4)	**2b**(BPh_4)	**2h**(BPh_4)	**2i**(BPh_4)	**2j**(BPh_4)	**2q**(BPh_4)
	Bond lengths							
Ru1–N1	2.0819(19)	2.0845(13)	2.0875(15)	2.080(2)	2.0746(14)	2.087(2)	2.0800(16)	2.085(2)
Ru1–N2	2.1199(17)	2.1080(13)	2.0991(15)	2.108(2)	2.1447(15)	2.165(2)	2.1379(17)	2.151(2)
Ru1–cymene[a]	1.6888(9)	1.6897(7)	1.6817(8)	1.6883(11)	1.6752(8)	1.6820(11)	1.6774(9)	1.6916(13)
Ru1–Cl1	2.3954(5)	2.3992(4)	2.4027(5)	2.3838(7)	2.4034(5)	2.4033(7)	2.3892(5)	2.4190(8)
	Bond angles							
N1–Ru1–N2	76.55(7)	76.21(5)	76.12(6)	76.57(8)	77.84(6)	77.52(8)	77.78(7)	77.15(8)
N1–Ru1–Cl1	87.61(5)	87.49(4)	89.48(4)	85.88(6)	82.56(4)	83.32(5)	81.75(5)	81.98(6)
N2–Ru1–Cl1	85.50(5)	87.09(4)	84.12(4)	84.50(6)	90.30(4)	90.79(5)	87.84(5)	91.02(6)
	Torsion angle							
N1–C5–C6–N2	0.7(3)	2.7(2)	7.2(2)	3.4(3)	11.0(2)	15.6(4)	14.7(3)	14.3(3)

[a] Distance between the Ru centre and the centroid of the η^6-coordinated cymene ligand.

2j(BPh_4) and **2q**(BPh_4). Their molecular structures in the solid state are presented in Figure 1, and characteristic parameters are summarized in Table 1. They all show a typical piano-stool geometry, in which the Ru^{II} centres adopt a distorted octahedral arrangement and are coordinated by a chelating 2-amino-4-(2-pyridinyl)pyrimidine ligand, an η^6-cymene ring and a terminal chlorido ligand.

The observed Ru–N1 (2.07–2.09 Å), Ru–cymene (1.67–1.69 Å) and Ru–Cl (2.40–2.42 Å) bond lengths are akin to those of related structures. In recently published molecular structures of compounds of the type [(η^6-arene)Ru(N,N′)-Cl]$^+$ (N,N′ = bidentate aromatic N-heterocycle), similar Ru–N (2.06–2.12 Å), Ru–(η^6-arene) (1.67–1.70 Å) and Ru–Cl (2.38–2.43 Å) bond lengths were reported.[19]

Further examination of the metric parameters given in Table 1 reveals that the Ru1–N1 (pyridine) bond length is always significantly shorter than the corresponding Ru1–N2 (pyrimidine) bond length, which proves that the pyridine moiety binds more strongly to the metal site than the pyrimidine donor. The electronic influence of the substituent in the 6-position of the pyrimidine ring on the lengths of the Ru1–N2 and the Ru–Cl bonds is negligible. In contrast, the introduction of a tertiary instead of a primary amino group into the 2-position of the pyrimidine ring leads to a pronounced elongation of the Ru1–N2 bond [e.g., **2a**(PF_6): 2.1199(17) vs. **2h**(BPh_4): 2.1446(15) and **2p**(BPh_4): 2.0992(15) vs. **2q**(BPh_4): 2.1509(19) Å]. Simultaneously, a pronounced increase of the N1–C5–C6–N2 torsion angle is found [lowest row in Table 1; e.g., **2a**(PF_6): 0.7(3) vs. **2h**(BPh_4): 11.0(2) and **2p**(BPh_4): 7.2(2) vs. **2q**(BPh_4): 14.3(3)°]. This is accomplished by a distortion of the pyrimidine ring and its amino substituent from planarity and leads to the conclusion that the bulky tertiary amino groups strongly interfere with the η^6-coordinated arene ligand. This results in steric strain and weakens the Ru1–N2 bond, which will play an important role in the following discussion on the mechanism of the transfer hydrogenation catalyzed by these complexes in the absence of an external base.

Transfer Hydrogenation

To prove whether these complexes follow a "bifunctional catalysis" mechanism, in other words, to elucidate whether the amino group takes part in the transfer-hydrogenation catalysis, we first focussed on ruthenium complexes bearing a primary amino group at the pyrimidine ring. The ruthenium(II) complex **2a**(Cl) (0.5 mol-%) was used to optimize the reaction conditions for the transfer hydrogenation of acetophenone in 2-propanol solution. A first series of experiments proved that this catalyst becomes active at ca. 82 °C (boiling 2-propanol) in the presence of KOH as the base. Evaluation of the optimum amount of base showed that with a base-to-catalyst ratio of 2.5:1 ca. 64% conversion can be observed after 3 h (Table 2, Entry 3). However, under these conditions the catalyst becomes inactive and will not reach 100% conversion, which is possible by increasing the base-to-catalyst ratio to 10:1 (Table 2, Entry 1). The catalyst shows no activity in the absence of the base.

Table 2. Optimization of the base (KOH) to catalyst ratio.[a]

Entry	Base/catalyst	Conversion [%] 3h	24 h
1	10:1	37	100
2	5:1	32	94
3	2.5:1	64	81
4	0:1	0	0

[a] Reaction conditions: acetophenone (2.5 mmol), **2a**(Cl) (1.25×10^{-2} mmol), 2-propanol (25 mL), 82 °C; the reactions were monitored by GC.

After the reaction conditions had been determined, the catalyst structure was optimized by changing (A) the counterion, (B) the substitution in the 5-position of the pyrimidine ring (R^3), and (C) the nature of the amine group (R^1, R^2; see Schemes 1 and 2). Table 3 summarizes the influence of the counterion in the series **2l**(X) (X = Cl^-, BF_4^-, PF_6^-, BPh_4^-). Although the differences are not pronounced, the weakly coordinating tetraphenylborate anion (Table 3, En-

try 4) clearly gives the best results at short and long reaction times.

Table 3. Effect of the counterion.[a]

Entry	Anion	Conversion [%] 2 h	6 h	24 h
1	Cl^-	28	60	100
2	BF_4^-	26	53	70
3	PF_6^-	45	69	78
4	$B(Ph)_4^-$	49	63	100

[a] Reaction conditions: acetophenone (2.5 mmol), **2l**(X) (1.25×10^{-2} mmol), 2-propanol (25 mL), 82 °C; the reactions were monitored by GC.

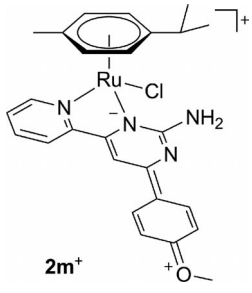
The substitution pattern on the pyrimidine ring was also changed. As summarized in Table 4, the substituent in the 5-position has a strong influence, which reflects that increased electron donation from the substituent results in an increase in catalytic activity. It is also clear that substituents with a π system, which will overlap with the pyrimidine π system, are beneficial.

Table 4. Influence of the substituent in the 5-position of the pyrimidine ring.[a]

Entry	Catalyst	Conversion [%] 2 h	6 h
1	**2a**(BPh_4)	19	35
2	**2l**(BPh_4)	49	63
3	**2k**(BPh_4)	69	89
4	**2p**(BPh_4)	73	87
5	**2m**(BPh_4)	79	98

[a] Reaction conditions: acetophenone (2.5 mmol), catalyst (1.25×10^{-2} mmol), 2-propanol (25 mL), 82 °C; the reactions were monitored by GC.

For the 6-*para*-methoxyphenyl function, the delocalization even includes the oxygen atom, which donates additional charge density to the nitrogen donor atom of the pyrimidine ring (Scheme 3). This reduces the strength of the Ru–Cl bond and, therefore, allows this ligand to be more easily replaced by an isopropanolato ligand, and subsequently a hydrido ligand is transferred to the Ru site.



Scheme 3.

A comparison of the bond lengths of **2a**(PF_6), **2k**(BPh_4) and **2p**(BPh_4) (Figure 1 and Table 1) with these data reveals that as the Ru1–N2 bond length decreases, or the Ru1–Cl1 bond length increases, the catalytic activity increases.

We have included [(η^6-cymene)Ru(Cl)(bipy)]$^+$Cl$^-$ (bipy = 2,2′-bipyridyl) in our study for comparison. Even with chloride as the counterion, this catalyst shows higher activities than **2a**(BPh_4), **2k**–**n**(BPh_4) and **2p**(BPh_4). Further comparison of these results with data from the literature suggested that the presence of the NH_2 group has a detrimental rather than positive effect on the catalytic performance of these systems. This leads to the conclusion that ligands **1a**(BPh_4), **1k**–**n**(BPh_4) and **1p**(BPh_4) will not take part in the catalytic process in terms of a "bifunctional mechanism". Therefore, we propose that similarly to Baratta's catalysts,[9] our ruthenium complexes follow an inner-sphere mechanism, whereby the alcohol and the ketone coordinate to the metal centre during the transformation. Similar results have been reported by Schlaf et al.[20] Their catalyst, which also carried an NH_2 group in close proximity to the metal site, did not show high activity. The authors explained this behaviour by either the high pK_a value of the NH_2 group or by a mismatch of the proton–hydride distance in the active species.

To overcome the drawbacks of the primary amino group in the 2-position of the pyrimidine ring, a series of catalysts were synthesized with either alkylamino or dialkylamino groups in this position (see Schemes 1 and 2). The results obtained in the catalytic transfer hydrogenation with these compounds are summarized in Table 5. Generally, the introduction of a tertiary amine group improves the activity dramatically. Contrary to the findings discussed above, electron-donating groups in the 4-position of the pyrimidine ring decrease the catalytic performance; the best result was found for the pyrrolidinyl-functionalized system **2i**(BPh_4) (Table 5, Entry 4). The compounds with an NHR moiety did not show better activities than the ones with a NH_2 moiety. We did not investigate the chiral ruthenium complexes **2f** and **2g** for their performance in enantioselective catalysis as they are mixtures of diasteromers.

Table 5. Effects of the amino group.[a]

Entry	Catalyst	Conversion [%] (time [min])	Entry	Catalyst	Conversion [%] (time [min])
1	**2o**(BPh_4)	45 (120)	4	**2i**(BPh_4)	97 (20)
2	**2q**(BPh_4)	48 (120)	5	**2c**(BPh_4)	100(600)
3	**2h**(BPh_4)	100 (90)	6	**2e**(BPh_4)	100 (600)

[a] Reaction conditions: acetophenone (2.5 mmol), catalyst (1.25×10^{-2} mmol), KOH (1.25×10^{-1} mmol), 2-propanol (25 mL), 82 °C; the reactions were monitored by GC.

Moreover, **2h**(BPh_4) and **2i**(BPh_4) were additionally investigated for their activity in the absence of base and achieved more than 80% conversion after 24 h, whereas the NH_2-functionalized catalyst **2a**(BPh_4) gave no conversion at all under these conditions. Although the reaction is definitively slower in the absence of KOH, this activity may become a clear benefit as it avoids corrosion and prevents side reactions of base-sensitive substrates. However, an alternative mechanism for the catalyst activation process has to be considered.

Mechanistic Investigations of the Transfer Hydrogenation in the Absence of an External Base

A base-free activation of the substrate is possible by an intramolecular C–H activation process at one of the ligands.

Chatani et al. reported the activation of C–H bonds adjacent to the nitrogen atom of an alkylamine group in ruthenium-catalyzed reactions,[21] and Whittlesey et al. reported a C–H activation at room temperature occurring at the N-heterocyclic carbene ligand in $Ru(IMes)(PPh_3)_2CO(H)_2$ (IMes = 1,3-dimesitylimidazol-2-ylidene) in the presence of a sacrificial alkene.[22] Here, the C–H-cleavage product readily reforms the starting dihydride upon reaction with H_2.[22a] This complex also catalyzes an indirect Wittig reaction, wherein the carbonyl substrate is generated by dehydrogenation of an alcohol.[22b] A reversible C–H bond activation process is crucial for both reactions.[22c] Very recently, Morris et al. presented the first iron-based transfer-hydrogenation catalyst that works without a base.[23] However, this catalyst is generated by first reacting a precursor with a strong base, isolating it and finally applying it in catalysis. These findings together with other reports[24] indicate that an intramolecular C–H activation in the ligand environment is likely to be the key step in the transfer hydrogenation with **2h**(BPh_4) and **2i**(BPh_4) in the absence of an external base. To better understand this behaviour, the following experiments were carried out.

First, catalytic amounts of **2i**(BPh_4) were treated with 1-phenylethanol in the absence and in the presence of KOH. Under both conditions, only traces of acetophenone were formed. This means that if a hydridoruthenium(II) species is formed, it cannot simply lose H_2. Otherwise ongoing dehydrogenation of 1-phenylethanol would occur. Second, to clarify whether **2i**(BPh_4) is capable of dehydrogenation of the alcohol stoichiometrically in the absence of both KOH and a hydrogen acceptor, it was reacted in a 1:2.5 ratio with 1-phenylethanol. After 24 h, 31% conversion of 1-phenylethanol to acetophenone was detected; this corresponds to about 80% of the **2i**(BPh_4) added in this experiment. This can be explained either by incomplete conversion or by reaching the equilibrium of the reaction. In any case, it indirectly proves the formation of a hydridoruthenium species, which is only possible by C–H activation. Third, the stoichiometric hydrogenation of acetophenone with **2c** (1.35:1 mixture, 24 h, 82 °C, toluene) in the absence of *i*PrOH was not feasible; this excludes a double C–H activation [e.g., of the $N(CH_2)_4$ moiety], which would follow a pathway discussed in the literature.[25]

To clarify the C–H activation process, electrospray mass spectrometry with collision-induced dissociation (CID) was applied (see Supporting Information). Under mild conditions (no CID), solely the corresponding cations **2a**$^+$, **2h**$^+$ and **2i**$^+$ were detected. Inducing fragmentation led to HCl elimination for all three complexes. For **2a**$^+$, the energy required for this process was considerably higher than for the *N*-alkylated compounds **2h**$^+$ and **2i**$^+$ (Figure 2). As the η^6-coordinated cymene ligand and the pyridine moiety are common features of all three ruthenium complexes, C–H activation at one of these sites should not result in pronounced differences in activities. Therefore, our efforts to locate the C–H activation site were concentrated on the pyrimidine ring. By introduction of a deuterium label to the 5-position of this ring (ligands [D_1]**1a** and [D_1]**1h**, Scheme 1),[26] the partially deuterated complexes [D]$_1$**2a** and [D]$_1$**2h** were obtained. For the cations [D]$_1$**2h**$^+$ and [D]$_1$**2h**$^+$, exclusive elimination of DCl (Figure 2) was observed in CID-MS, which proves that C–H activation occurs selectively at the 5-position of the pyrimidine ring.

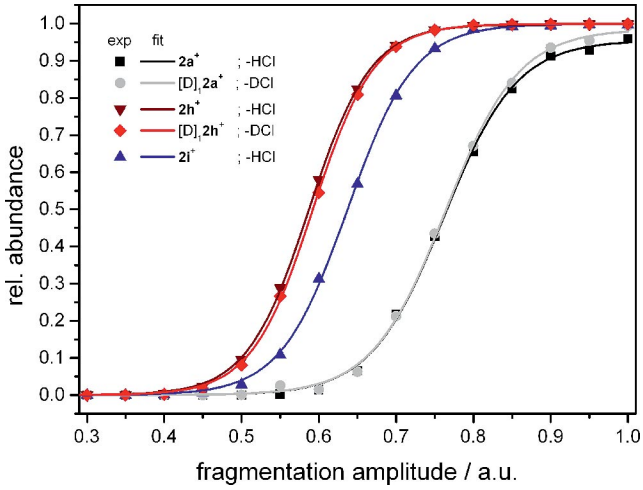


Figure 2. Collision-induced fragmentation of the cations **2a**$^+$ (black filled square), [D]$_1$**2a**$^+$ (grey filled circle), [D]$_1$**2h**$^+$ (upside-down filled red triangle), [D]$_1$**2h**$^+$ (red diamond) and **2i**$^+$ (blue triangle).

DFT calculations allowed a further evaluation of this process: elimination of HCl from the cations **2a**$^+$, **2h**$^+$ and **2i**$^+$ starts by breaking of the Ru–N(pyrimidine) bond and follows a so-called roll-over metalation mechanism.[27] The results on the C–H activation process are exemplarily shown for **2h**$^+$ in Figure 3 (for complete DFT results, see the Supporting Information). To elucidate the role of both the aminogroup and the pyrimidine moiety, we have also calculated this mechanism for the corresponding ruthenium(II) complexes **3**$^+$ and **4**$^+$ with a 2-(pyrimidine-4-yl)-pyridine and a 2,2′-bipyridine ligand, respectively. The data (ΔH_f) for the HCl elimination show that all energies are about 9–17 kcal/mol higher for **2a**$^+$, **3**$^+$ and **4**$^+$ than for **2h**$^+$ and **2i**$^+$ (Table 6). The energies calculated for **2h**$^+$ are slightly lower than the energies for **2i**$^+$. As these energy differences are already found for TS1, the breaking of the Ru–N(pyrimidine) bond is crucial for the C–H activation. We assign these differences in bond energies in the order **2a**$^+$ >> **2i**$^+$ > **2h**$^+$ to an increase of steric hindrance with the cymene ligand when the NH_2 group (**2a**$^+$) is substituted by an NR_2 group (**2h**$^+$ and **2i**$^+$). The catalytic activities follow the order **2a**(BPh_4) << **2h**(BPh_4) < **2i**(BPh_4); the inversed order of **2h**(BPh_4) and **2i**(BPh_4) may be because of solvent or counterion effects. There are further slight differences between **2a**$^+$ on one side and **3**$^+$ and **4**$^+$ on the other, which allow us to get a deeper insight into the role of the amino group: First the energies of TS1 are about 3–4 kcal/mol lower for **3**$^+$ and **4**$^+$ than for **2a**$^+$, which can be explained by a certain stabilization of the starting structure **A** owing to π donation from the NH_2 group. This agrees with a stabilization (approx 5 kcal/mol) of the π-complex-like structure **B** for **2a**$^+$ with respect to those of **3**$^+$ and **4**$^+$. Looking at

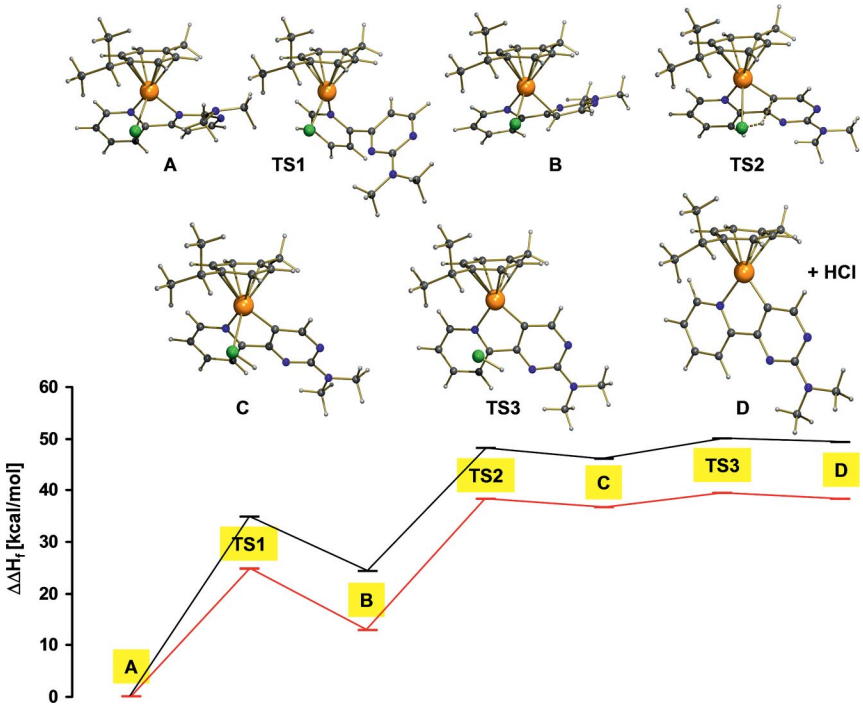


Figure 3. Calculated geometries leading to the elimination of HCl from the cation **2h**$^+$; calculated enthalpies $\Delta\Delta H_f$ [kcal/mol] for the cations **2h**$^+$ (red line) and **2a**$^+$ (black line).

Table 6. Calculated heats of formation ($\Delta\Delta H_f$), enthalpies ($\Delta\Delta H$) and Gibbs energies ($\Delta\Delta G$) of the C–H activation steps [kcal/mol].

Step	**2a**$^+$	**2h**$^+$	**2i**$^+$	**3**$^+$	**4**$^+$
A	0.00/0.00/0.00	0.00/0.00/0.00	0.00/0.00/0.00	0.00/0.00/0.00	0.00/0.00/0.00
TS1	34.81/33.66/32.11	24.64/23.60/20.92	25.29/24.28/22.56	31.04/30.09/29.34	31.84/30.84/30.31
B	24.32/23.86/23.21	12.89/12.47/10.13	12.99/12.68/11.55	29.11/28.77/27.08	29.50/29.03/27.78
TS2	48.11/43.56/42.76	38.20/33.93/31.81	38.52/34.35/32.97	49.90/44.88/44.63	51.15/46.06/45.74
C	45.94/43.17/40.92	36.66/34.00/30.46	37.11/34.56/32.39	44.29/41.65/40.02	46.34/43.62/42.29
TS3	50.03/46.54/40.98	39.43/36.09/31.20	39.81/36.53/32.01	not found	not found
D	49.22/45.36/32.78	38.17/34.47/20.98	38.49/34.75/21.27	52.06/48.19/36.44	53.66/49.64/37.87

the energies of the final 16 valence electron (VE) structure **D**, it becomes clear that again π interactions between the carbanion and the ruthenium(II) centre stabilize **2a**$^+$ with respect to **3**$^+$ and **4**$^+$ by a few kcal/mol.

It is possible to calibrate the internal voltage scales of the mass spectrometers fragmentation amplitudes towards appearance energies ($E_{50\%}$) of the fragment ions by means of substituted benzylpyridinium ions ("thermometer ions").[28] The precision of such an approach is compromised if additional fragmentation channels are taken into account.[28b] With **2a**$^+$, **2h**$^+$ and **2i**$^+$ this analysis resulted in an excellent correlation between the calculated activation energies (TS3, Figure 4) and the fitted energies from the CID experiments (loss of HCl or DCl, Table 7).

To trap and characterize some of the intermediates, a further series of experiments was performed. When an NMR sample of **2i**(BPh_4) in $CDCl_3$ is heated to 60 °C for 15 h, a new singlet at δ = 7.36 ppm is found and can be assigned to benzene, which forms from protodeborylation of the tetraphenylborate anion because of the release of HCl in the C–H activation process.[29] This reaction is sup-

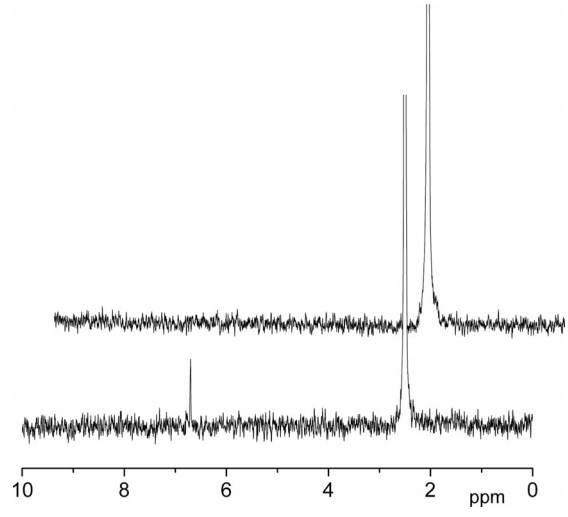


Figure 4. ^{2}H NMR spectra of [D_1]**2h**(BPh_4) in $HOCH(CH_3)_2$ before (bottom) and after (top) heating to 80 °C for 1 h; the signal at δ = 2.6 ppm is from [D_6]DMSO, applied as an internal standard in a sealed glass capillary.

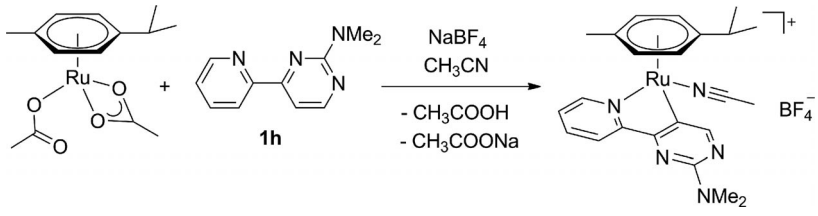
Table 7. Enthalpies of cations **2a**$^+$, **2h**$^+$ and **2i**$^+$ and of the deuterated systems [D$_1$]**2a**$^+$ and [D$_1$]**2h**$^+$ ($\Delta\Delta H_{fit}$) estimated from a linear fit function of benzylpyridinium ions ($\Delta\Delta H_{calc}$ vs. CID $E_{50\%}$ value) and calculated ZPE-corrected enthalpies ($\Delta\Delta H$) of the transition state TS3 of the HCl loss.

Species	**2a**$^+$	[D$_1$]**2a**$^+$	**2h**$^+$	[D$_1$]**2h**$^+$	**2i**$^+$
$\Delta\Delta H_{fit}$ [kcal/mol]	49	49	34	35	36
$\Delta\Delta H$ [kcal/mol]	46.5	–	36.1	–	36.5

pressed by the addition of AgOAc, which captures the acid, or when the solvent is CD_3OD, which reduces the acidity of HCl by solvation. To finally elucidate the influence of the counteranion on the activation process, catalytic transfer-hydrogenation reactions with different aliquots of sodium tetraphenylborate were conducted in 2-propanol. The addition of 1 equiv. of sodium tetraphenylborate caused the yield to drop to 30% (after 4 h). Two equivalents inhibited the reaction completely; no conversion was observed after 4 h. Therefore, we can exclude that the tetraphenylborate anion acts as the base in the transfer-hydrogenation mechanism.

A hydrido ruthenium complex was expected to be trapped by heating **2i**(BPh_4) and $NaBH_4$ in dry methanol at reflux for 15 h. However, no peaks with a chemical shift below δ = 0 ppm, typical for metal hydrido species, could be detected Therefore, the fate of the deuterated species [D$_1$]-**2i**(BPh_4) in 2-propanol solution was followed by means of ^{2}H NMR spectroscopy. The deuterium atom at the 5-position of the pyrimidine ring gives a resonance at δ = 6.70 ppm in the ^{2}H NMR spectrum (Figure 4). This signal disappeared when the sample was heated for 1 h at 80 °C; this is a clear hint for a D/H exchange under the conditions of the transfer hydrogenation in the absence of an external base.

Additionally, the formation of the *C*,*N*-coordinated (η^6-cymene)Ru complex could be proved. By reacting the ruthenium precursor (η^6-cymene)Ru(OAc)$_2$[30] with **1h** (Scheme 4) in the presence of sodium tetrafluoroborate in acetonitrile, quantitative conversion was observed by ^{1}H NMR spectroscopy (Figure 5). The resonance of the 1-H proton (for numbering, see Scheme 2) of the pyridine ring is shifted to lower field, which indicates a loss of electron density at the Ru centre. The two doublets of the pyrimidine protons 7-H and 8-H in the nonactivated complex disappeared; 8-H in the activated complex gives a singlet at δ = 8.95. We assume that one molecule of acetonitrile is coordinated to the Ru centre. The ESI mass spectra of these solu-



Scheme 4. Formation of the C–H-activated species.

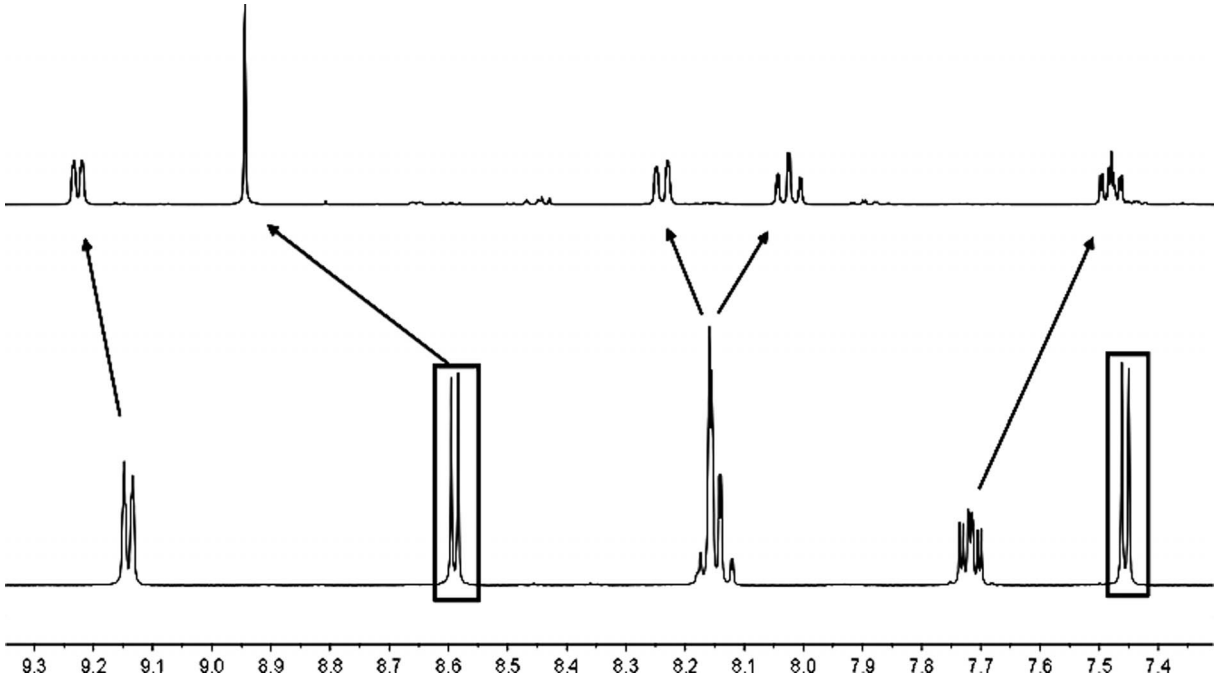
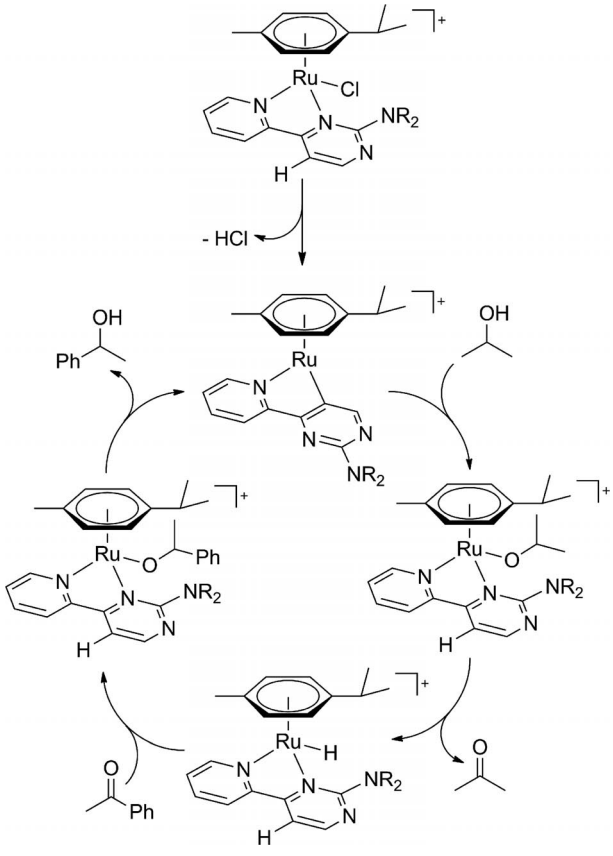


Figure 5. Aromatic region of the ^{1}H NMR spectra of the nonactivated (bottom) and the C–H-activated complex (top).

tions show signals for the C–H-activated cation with and without one molecule of acetonitrile.

Recently, we showed that dichloropalladium(II) complexes of (2-aminopyrimidin-4-yl)triphenylphosphanes exhibit a similar pattern of reactivity: as long as there is a primary amine at the pyrimidine ring, the ligand undergoes *P,N*-coordination. Switching to a tertiary amine, results in C–H activation at the pyrimidine ring, and the ligand employs a *P,C*-coordination mode.[31] Depending on the substitution pattern, the resulting palladium complexes show large differences in their catalytic activities. Here, we were able to characterize both modes of coordination by NMR spectroscopy and X-ray structure analysis.

By combining the results of the ESI-MS measurements, the DFT calculations, the catalytic experiments and the results obtained with the (η^6-cymene)$Ru(OAc)_2$ precursor, we propose the formation of the catalytically active species by C–H activation in the absence of the base (Scheme 5). A carbon-centred internal base is formed and activates *i*PrOH to start the catalytic cycle.



Scheme 5. Proposed reaction mechanism, wherein catalyst activation by C–H bond cleavage leads to a transfer hydrogenation in the absence of an external base.

Conclusions

Until now, ruthenium(II) complexes have been the most active systems for the transfer hydrogenation of ketones. However, the presence of a base to activate the precatalyst seemed to be unavoidable. In this work, we found that by slight variation of the functional group attached to a nitrogen donor ligand, the first phosphane-free and air-stable transfer-hydrogenation catalysts are accessible and that they work even in the absence of a base. The key step in the catalyst self-activation process is a C–H bond cleavage at the pyrimidine part of the bidentate nitrogen donor ligand, which thus switches from a *N,N*- to a *C,N*-coordination mode. This activation process is strongly supported by NMR spectroscopy, kinetic studies, ESI-MS combined with collision-induced dissociation (CID) and DFT calculations. We are presently examining other transition-metal-catalyzed reactions with catalysts bearing aminopyrimidine-based ligands to prove the general applicability of these C–H activation processes in catalysis.

Experimental Section

General: All chemicals for the syntheses of the ligands were purchased from Sigma–Aldrich or Acros Organics, and [(η^6-cymene)-$Ru(Cl)(\mu^2\text{-}Cl)]_2$ was obtained from Strem Chemicals. Solvents for the ligand syntheses were used without further purification, solvents for the synthesis of ruthenium complexes and for catalytic experiments were dried prior to use by standard methods. ^1H and ^{13}C NMR spectra were recorded with two Bruker Spectrospin Avance devices with resonance frequencies of 400 or 600 MHz and 151 or 101 MHz for the ^1H or ^{13}C nuclei, respectively. The IR spectra with a resolution of $\pm 2\ cm^{-1}$ were recorded with a Perkin–Elmer FT-ATR IR 1000 spectrometer equipped with a diamond coated ZnSe window. The elemental analyses were performed at the Fachbereich Chemie. For the ligand syntheses, three different methods were applied depending on the substitution pattern of the pyrimidine ring. Those methods are exemplarily described for the synthesis of **1a**, **1k** and **1p**. The analytic data for all compounds are given in the Supporting Information.

2-Amino-4-(pyridin-2-yl)pyrimidine (1a, Method 1): Sodium (1 g, 43.5 mmol) was added to a solution of guanidinium carbonate (1.8 g, 18.3 mmol) in dried EtOH (20 mL) under an atmosphere of nitrogen. After the sodium had dissolved, (*E*)-1-(2-pyridinyl)-3-dimethylaminoprop-2-enone[32] (3 g, 17 mmol) was added, and the solution was heated to reflux for 24 h. After evaporation of the solvent, the residue was washed with ice-cooled water several times, and the product was recrystallized from CH_2Cl_2/Et_2O, yield 2.34 g (80%). $C_9H_8N_4$ (172.19): calcd. C 62.78, H 4.68, N 32.54; found C 62.48, H 4.68, N 31.87. ^1H NMR (400.1 MHz, [D$_6$]DMSO, 20 °C): δ = 8.68 (d, $J_{H,H}$ = 4.3 Hz, 1 H, 1-H), 8.41 (d, $J_{H,H}$ = 4.7 Hz, 1 H, 8-H), 8.32 (d, $J_{H,H}$ = 8.22 Hz, 1 H, 4-H), 7.93 (m, 1 H, 3-H), 7.49–7.45 (m, 2 H, 2-H and 7-H), 6.79 (br s, 2 H, NH_2) ppm. ^{13}C NMR (400.1 MHz, [D$_6$]DMSO, 20 °C): δ = 163.78 (s, C-9), 162.94 (s, C-6), 159.48 (s, C-8), 154.04 (s, C-5), 149.41 (s, C-1), 137.24 (s, C-3), 125.34 (s, C-4), 120.75 (s, C-2), 105.97 (s, C-7) ppm.

2-Amino-4-phenyl-6-(pyridin-2-yl)pyrimidine (1k, Method 2): (*E*)-3-Phenyl-1-(pyridin-2-yl)prop-2-en-1-one[33] (1.67 g, 8 mmol) was added to a solution of guanidinium carbonate (2.35 g, 24 mmol) in EtOH (25 mL). The reaction mixture was heated to reflux for 24 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2. The organic phase was washed three times with water and dried with $MgSO_4$. Yellow crystals were obtained from a CH_2Cl_2/hexane solution after 1 d in a refrigerator, yield 1.82 g (92%). $C_{15}H_{12}N_4$ (248.29): calcd. C 72.56, H 4.87, N 22.57; found C 71.48,

H 4.91, N 22.54. ^{1}H NMR (400.1 MHz, [D$_6$]DMSO, 20 °C): δ = 8.75 (d, $J_{H,H}$ = 4.3 Hz, 1 H, 1-H), 8.39 (d, $J_{H,H}$ = 7.83 Hz, 1 H, 4-H), 8.16–8.13 (m, 2 H, 11-H), 8.06 (s, 1 H, 7-H), 7.95 (m, 1 H, 3-H), 7.6–7.4 (m, 4 H, 2-H, 12-H, 13-H), 6.92 (s br, 2 H, NH$_2$) ppm. ^{13}C NMR (400.1 MHz, [D$_6$]DMSO, 20 °C): δ = 165.25 (s, C-6), 164.14 (s, C-8), 164.10 (s, C-9), 154.17 (s, C-5), 149.37 (s, C-1), 137.29 (s, C-10), 137.24 (s, C-3), 130.50 (s, C-13), 128.74 (s, C-12), 126.80 (s, C-11), 125.36 (s, C-4), 120.96 (s, C-2), 101.76 (s, C-7) ppm.

2-Amino-4-*tert*-butyl-6-(pyridin-2-yl)pyrimidine (1p, Method 3): Sodium (0.2 g, 8 mmol) was added to a solution of guanidinium carbonate (0.8 g, 8 mmol) in dried EtOH (25 mL) under an atmosphere of nitrogen. 4,4-Dimethyl-1-pyridin-2-yl-pentane-1,3-dione[34] (1.64 g, 8 mmol) was added to the solution, which was then heated to reflux for 24 h. After evaporation of the solvent, the residue was washed with cold water, and the product was recrystallized from EtOH, yield 0.55 g (30%). $C_{13}H_{16}N_4$ (228.30): calcd. C 68.39, H 7.06, N 24.54; found C 68.18, H 6.97, N 24.13. ^{1}H NMR

Table 8. Summary of the crystallographic data and details of data collection and refinement for **2a**(PF$_6$), **2k**(BPh$_4$), **2p**(BPh$_4$), **2b**(BPh$_4$), **2h**(BPh$_4$), **2i**(BPh$_4$), **2j**(BPh$_4$) and **2q**(BPh$_4$).

	2a(PF$_6$)	**2k**(BPh$_4$)	**2p**(BPh$_4$)	**2b**(BPh$_4$)
Empirical formula	$C_{21}H_{28}ClF_6N_4OPRu$	$C_{49}H_{46}BClN_4Ru$	$C_{53}H_{65}BClN_4O_{1.5}Ru$	$C_{47}H_{50}BCl_3N_4Ru$
Formula weight	633.96	838.23	929.42	889.14
Crystal size [mm]	0.28 × 0.21 × 0.18	0.20 × 0.13 × 0.08	0.40 × 0.17 × 0.13	0.16 × 0.08 × 0.06
T [K]	150(2)	150(2)	150(2)	150(2)
λ [Å]	1.54184	1.54184	1.54184	1.54184
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	10.3751(1)	13.5219(1)	15.2326(1)	12.89110(10)
b [Å]	15.0288(2)	21.5269(2)	13.8012(1)	14.90500(10)
c [Å]	16.0810(2)	14.0468(1)	24.5075(2)	22.7354(2)
α [°]	90	90	90	90
β [°]	102.954(1)	90.424(1)	107.188(1)	98.3670(10)
γ [°]	90	90	90	90
V [Å^3]	2442.77(5)	4088.70(6)	4922.07(6)	4321.93(6)
Z	4	4	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.724	1.362	1.254	1.366
μ [mm^{-1}]	7.452	4.002	3.392	4.925
θ range [°]	4.08–62.64	3.76–62.64	3.04–62.65	3.47–62.67
Reflections collected	17462	31505	40936	33782
Independent reflections	3903 (R_{int} = 0.0274)	6538 (R_{int} = 0.0241)	7866 (R_{int} = 0.0225)	6916 (R_{int} = 0.0299)
Data/restraints/parameters	3903/2/327	6538/2/514	7866/40/580	6916/1/512
Final R ind. [$I > 2\sigma(I)$][a]	0.0230, 0.0589	0.0200, 0.0529	0.0244, 0.0647	0.0292, 0.0796
R ind. (all data)[b]	0.0245, 0.0596	0.0225, 0.0535	0.0264, 0.0655	0.0346, 0.0815
GooF[c]	1.079	1.034	1.042	1.045
$\Delta\rho_{max}/_{min}$ [e Å^{-3}]	0.319/–0.618	0.227/–0.360	0.414/–0.335	0.679/–0.944
	2h(BPh$_4$)	**2i**(BPh$_4$)	**2j**(BPh$_4$)	**2q**(BPh$_4$)
Empirical formula	$C_{45}H_{46}BClN_4Ru$	$C_{48}H_{49}BCl_4N_4Ru$	$C_{48}H_{50}BClN_4Ru$	$C_{49}H_{54}BClN_4Ru$
Formula weight	790.19	935.59	830.25	846.29
Crystal size [mm]	0.18 × 0.12 × 0.11	0.05 × 0.09 × 0.11	0.18 × 0.07 × 0.03	0.25 × 0.09 × 0.05
T [K]	150(2)	150(2)	150(2)	150(2)
λ [Å]	1.54184	1.54184	1.54184	1.54184
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	13.0910(2)	9.3478(2)	12.2710(1)	14.6567(3)
b [Å]	11.8941(1)	24.5559(5)	14.9669(1)	9.6078(2)
c [Å]	25.6986(3)	19.0534(5)	22.3485(2)	33.5405(6)
α [°]	90	90	90	90
β [°]	95.960(1)	90.376(2)	95.163(1)	100.226(2)
γ [°]	90	90	90	90
V [Å^3]	3979.79(8)	4373.49(17)	4087.85(6)	4648.10(16)
Z	4	4	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.319	1.421	1.349	1.209
μ [mm^{-1}]	4.076	5.446	3.994	3.521
θ range [°]	3.46–62.74	2.9–62.7	3.56–62.65	3.06–62.63
Reflections collected	31463	47086	32737	24700
Independent reflections	6363 (R_{int} = 0.0237)	7017 (R_{int} = 0.053)	6515 (R_{int} = 0.0336)	7402 (R_{int} = 0.0367)
Data/restraints/parameters	6363/0/474	7017, 0, 526	6515/0/499	7402/0/513
Final R ind. [$I > 2\sigma(I)$][a]	0.0218, 0.0562	0.0253, 0.0583	0.0245, 0.0652	0.0310, 0.0771
R ind. (all data)[b]	0.0240, 0.0570	0.0373, 0.0697	0.0293, 0.0665	0.0390, 0.0797
GooF[c]	1.041	0.95	1.045	0.946
$\Delta\rho_{max}/_{min}$ [e Å^{-3}]	0.292/–0.597	0.42/–0.46	0.536/–0.388	0.402/–0.581

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

(400.1 MHz, [D$_6$]DMSO, 20 °C): δ = 8.70 (d, $J_{H,H}$ = 3.92 Hz, 1 H, 1-H), 8.30 (d, $J_{H,H}$ = 8.22 Hz, 1 H, 4-H), 7.93 (m, 1 H, 3-H), 7.56 (s, 1 H, 7-H), 7.47 (m, 1 H, 2-H), 6.60 (s br, 2 H, NH_2), 1.27 (s, 9 H, 11-H) ppm. ^{13}C NMR (400.1 MHz, [D$_6$]DMSO, 20 °C): δ = 179.18 (s, C-8), 163.46 (s, C-6), 163.16 (s, C-9), 154.43 (s, C-5), 149.28 (s, C-1), 137.19 (s, C-3), 125.13 (s, C-4), 120.78 (s, C-2), 101.02 (s, C-7), 37.13 (s, C-10), 29.19 (s, C-11) ppm.

General Synthesis of the Ruthenium(II) Complexes [(η^6-*p*-cymene)-RuCl(L)]X: A solution of the appropriate ligand (0.32 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of [(η^6-*p*-cymene)$RuCl_2]_2$ (91.86 mg, 0.15 mmol) in CH_2Cl_2 (20 mL). The solution was stirred for 20 h at room temperature and then concentrated, and the product was precipitated by adding Et_2O (10 mL). The product was collected by filtration, washed with Et_2O twice and dried in vacuo. For ruthenium complexes with other counteranions, a threefold excess of KPF_6, $NaBF_4$ or $NaBPh_4$ was added to the solution. Before the solution was concentrated, the excess KPF_6, $NaBF_4$ or $NaBPh_4$ and the other formed salts were removed by filtration.

X-ray Structure Analyses: The crystal data and refinement parameters for **2a**(PF_6), **2k**(BPh_4), **2p**(BPh_4), **2b**(BPh_4), **2h**(BPh_4), **2i**(BPh_4), **2j**(BPh_4) and **2q**(BPh_4) are collected in Table 8. The structures were solved by direct methods (SIR92[35]), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures.[36] Semi-empirical absorption corrections from equivalents (Multiscan) were performed.[37] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to the nitrogen atoms were located in the difference Fourier synthesis and were refined semi-freely with the help of a distance restraint and their *U* values were constrained to 1.2 times the *U*(eq) value of the attached nitrogen atoms. All other hydrogen atoms were placed in calculated positions and refined by using a riding model. The SQUEEZE process integrated in PLATON has been used for **4c** because of the existence of severely disordered solvent molecules (probably a mixture of pentane, CH_2Cl_2/$CHCl_3$, and H_2O).

CCDC-934261 [for **2a**(PF_6)], -934262 [for **2k**(BPh_4)], -934263 [for **2p**(BPh_4)], -934264 [for **2b**(BPh_4)], -934265 [for **2h**(BPh_4)], -934266 [for **2i**(BPh_4)], -934267 [for **2j**(BPh_4)] and -934268 [for **2q**(BPh_4)] 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.

ESI-MS Experiments: Electrospray ionization mass spectrometry (ESI-MS) was performed with a Bruker Esquire 3000plus ion-trap instrument. The ion source was used in positive electrospray ionization mode. The scan speed was 13000 *m*/*z*/s in normal resolution scan mode (0.3 FWHM/*m*/*z*), and the scan range was at least 50 to 2800 *m*/*z*. All spectra were accumulated for at least two minutes. Sample solutions in acetonitrile (HPLC grade) at concentrations of 1×10^{-4} M were continuously infused into the ESI chamber at a flow rate of 4 μL/min by using a syringe pump. Nitrogen was used as the drying gas with a flow rate of 3.0 L/min at 300 °C. The solutions were sprayed at a nebulizer pressure of 4 psi (275.8 mbar), and the electrospray needle was typically held at 4.5 kV. The instrument was controlled by Bruker Esquire Control 5.3 software, and data analysis was performed by using Bruker Data Analysis 3.4 software.

Quantum Chemical Calculations: Quantum chemical calculations on **2a**$^+$, **2h**$^+$, **2i**$^+$, **3**$^+$ and **4**$^+$ were performed with the Gaussian03[38] program by using the B3LYP gradient-corrected exchange-correlation functional in combination with the 6-31G* basis set for C, H, N, Cl and the Stuttgart/Dresden ECP basis set for Ru.[39] Full geometry optimizations were carried out in C_1 symmetry by using analytical gradient techniques, and the resulting structures were confirmed to be true minima by diagonalization of the analytical Hessian matrix. The starting geometries for the calculations of **2a**$^+$, **2h**$^+$, **2i**$^+$, **3**$^+$ and **4**$^+$ were taken from solid-state structures of appropriate compounds. Different orientations of the cymene ligand were not taken into account. This may lead to small variations of the calculated energies.

Supporting Information (see footnote on the first page of this article): X-ray structure analyses of **1m**, **1p** and **1q**. Analytical data for all compounds.

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