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Cationic and neutral ruthenium(II) complexes containing both arene or Cp* and functionalized aminophosphines. Application to hydrogenation of aromatic ketones

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ABSTRACT

Hydrogen transfer reduction processes are attracting increasing interest from synthetic chemists in view of their operational simplicity. For this aim, a series of novel Ru(II) complexes with the P—N—P ligands were synthesized starting from the complex $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ or [RuCp*Cl(COD)]. The complexes were fully characterized by analytical and spectroscopic methods. $^{31}P\{^1H\}$ NMR, DEPT, ^1H–^{13}C HETCOR or ^1H–^1H COSY correlation experiments were used to confirm the spectral assignments. Complexes **5**, **6** and **7** catalyze the transfer hydrogenation of acetophenone derivatives to 1-phenylethanol derivatives in the presence of *iso*-PrOH as the hydrogen source. Catalytic studies showed that all complexes are excellent catalytic precursors for the transfer hydrogenation of acetophenone derivatives in 0.1 M *iso*-PrOH solution. Notably **5** acts as an excellent catalyst giving the corresponding alcohols in excellent conversions up to 99% (TOF $\leq$ 492 h^{-1}).

1. Introduction

Aminophosphines and bis(phosphino)amines with P—NH and P—N—P skeletons respectively, have proved to be much more versatile ligands, and varying the substituents on both the P- and N-centres gives rise the changes in the P—N—P angle and the conformation around the P-centres [1–3]. Small variations in these ligands can cause significant changes in their coordination behaviour and the structural features of the resulting complexes [4,5]. Aminophosphine ligands have been studied for the last three decades and found to be of considerable interest due their wide range of applications in organometallic chemistry for the development of industrial processes involving a great number of catalytic reactions [6]. A large number of complexes with aminophosphine ligands have been evaluated in different catalytic reactions including allylic alkylation [7], amination [8], Heck [9] Sonogashira [10], Suzuki [11], hydroformylation [12], hydrogenation [13] and polymerization [14] reactions. Some aminophosphines and derivatives have also found application as anticancer drugs [15], herbicides and antimicrobial agents, as well as neuroactive agents [16].

Transfer hydrogenation using ruthenium complexes as catalysts has been an increasingly useful tool in organic synthesis [17–19], allowing transformations otherwise very difficult or almost impossible to carry out. Catalytic transfer hydrogenation with the aid of a stable hydrogen donor is a useful alternative method for catalytic hydrogenation by molecular hydrogen [20,21]. In transfer hydrogenation, organic molecules such as primary and secondary alcohols [22] or formic acid and its salts [23] have been employed as the hydrogen source. The use of the hydrogen donor has some advantages over the use of molecular hydrogen since it avoids no risks and the constrains associated with hydrogen gas as well as the necessity for pressure vessels and other equipments. 2-propanol is a popular reactive solvent for transfer hydrogenation reactions since it is easy to handle and is relatively non-toxic, environmentally benign and inexpensive. The volatile acetone by-product can also be easily removed to shift unfavourable equilibria.

We previously reported the preparation of the $(PPh_2)_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2$, **3** and $(PPh_2)_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2$, **4** [24]. Now we have extended our studies to include ruthenium as a central metal [25–29]. Herein we wish to report the synthesis of Ru(II) complexes $[Ru((Ph_2P)_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2)(\eta^6\text{-}p\text{-cymene})Cl]Cl$, **5**, $[Ru((Ph_2P)_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2)(\eta^6\text{-}p\text{-cymene})Cl]Cl$, **6** and $[RuCp^*((Ph_2P)_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2)Cl]$, **7** and their application in the transfer hydrogenation of aromatic ketones.

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2. Results and discussion

2.1. Synthesis and characterization of the metal complexes

We have previously described [24] the synthesis of *N,N*-bis (diphenylphosphino)isopropylanilines, $(PPh_2)_2N{-}C_6H_4{-}CH(CH_3)_2$, having isopropyl substituent at the carbon 2- (**3**) or 4- (**4**) easily prepared from the reaction of $H_2N{-}C_6H_4$-2-$CH(CH_3)_2$, (**1**) or $H_2N{-}C_6H_4$-4-$CH(CH_3)_2$, (**2**) respectively, with two equivalents of chlorodiphenylphosphine in the presence of triethylamine in thf solution. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ which was prepared from the reaction of the commercially available α-phellandrene(5-isopropyl-2-methylcyclohexa-1,3-diene) with $RuCl_3$ [30] was initially chosen as a starting material for the synthesis of ruthenium(II) complexes **5** and **6**. The whole reactions carried out with $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ are depicted in Scheme 1.

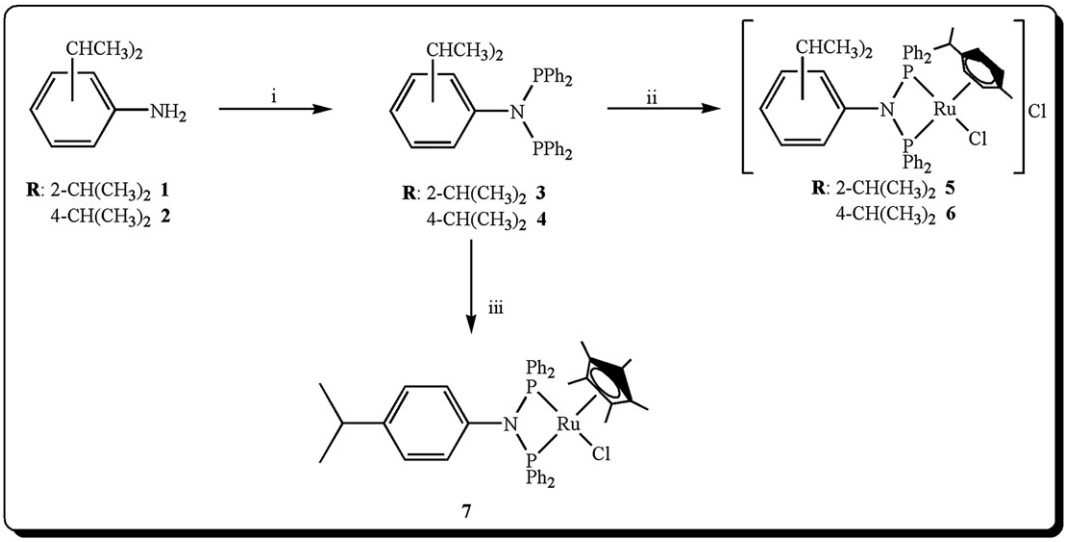
Complexation reactions were straightforward, with coordination to ruthenium being carried out at room temperature. Treatment of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ with one equivalent of $(PPh_2)_2N$-C_6H_4-2-$CH(CH_3)_2$, (**3**) or $(PPh_2)_2N$-C_6H_4-4-$CH(CH_3)_2$, (**4**) affords the corresponding mono bis(chelate) complexes in high yield as the main products, respectively (Fig. 1). The initial color change, i.e., from clear orange to deep red [31], attributed to the dimer cleavage most probably by the bis(phosphino)amine ligand. The $^{31}P{-}\{^1H\}$ NMR spectra are quite consistent with the structures [32], that of containing **5** or **6**. Furthermore, ^1H NMR and ^{13}C NMR spectral data of **5** and **6** are consistent with the structure proposed (for details see Experimental section). ^1H NMR spectra of complexes display signals of the η^6-*p*-cymene ligand together with the resonances of the hydrogens of the P-coordinated ligands. The arene signals are well resolved and show only H–H coupling, as found in previously reported mononuclear p-cymene compounds [33–36]. Furthermore, $^{13}C{-}\{^1H\}$ NMR spectra of complexes **5** and **6** display resonances that are consistent with a P-coordination of ligands. The structural composition of the complex has also been confirmed by IR and elemental analysis.

The reaction of [RuCp*Cl(COD)] with $(PPh_2)_2N$-C_6H_4-4-$CH(CH_3)_2$ in thf in a ratio 1:1 at r.t. for 3 h gave a red micro crystalline precipitate of neutral complex $[RuCp^*((Ph_2P)_2N{-}C_6H_4$-4-$CH(CH_3)_2)Cl]$ (**7**) (Scheme 1). The $^{31}P{-}\{^1H\}$ NMR spectrum of **7** shows a single resonance at 89.28 ppm, in line with the values previously observed for similar compounds [37,38], indicating that the diene (COD) has been replaced by the bidendate chelating bis(phosphino)amine. But, attempts to prepare $[RuCp^*((Ph_2P)_2N{-}C_6H_4$-2-$CH(CH_3)_2)Cl]$ did not succeed, may be, due to the steric repulsion of the *o*-position isopropyl group. In the $^{31}P{-}\{^1H\}$ NMR spectra, two singlet were observed. ^1H and ^{13}C NMR spectra of compound **7** display all signals of coordinated ligand and are in agreement with the structures proposed (for details see Experimental section). Elemental analysis of product **7** is consistent with the suggested molecular formulas.

2.2. Catalytic transfer hydrogenation of acetophenone derivatives

The activity of Ru(II) arene complexes is well known in this catalytic process ([39–43] and references therein). Recently, we have reported that the complexes, based on the ligands with P–N, P–O and P–N–P backbone, are active catalysts in the reduction of aromatic ketones [44,45]. The observed activity of these complexes has encouraged us to investigate other analogous ligands and other transition metal complexes of these ligands [46,47]. So, the catalytic activity of complexes **5**, **6** and **7** in transfer hydrogenation of aromatic ketones by *iso*-PrOH was investigated (Scheme 2). In all the reactions, these complexes catalyzed the reduction of ketones to the corresponding alcohols via hydrogen transfer from *iso*-PrOH. In a typical experiment, 0.01 mmol of the complex and 1 mmol of acetophenone were added to a solution of NaOH in *iso*-PrOH (0.05 mmol of NaOH in 10 mL *iso*-PrOH) and refluxed at 82 °C, the reaction being monitored by GC. With a complex/NaOH ratio of 1/5, the complexes are very active, which leads to a quantitative transformation of the acetophenone, with a good TOF of $<492\ h^{-1}$.

In a preliminary study, the synthesized complexes **5**–**7** were evaluated as a precursor for the catalytic transfer hydrogenation of the acetophenone by iso-PrOH/NaOH as a reducing system and the results are summarized in Table 1. At room temperature no appreciable formation of 1-phenylethanol was observed (Table 1, Entries 1, 2 and 3) and also the catalytic activity of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ under the applied experimental conditions is negligible. In addition, as can be inferred from the Table 1 (Entries 4, 5 and 6), the precatalysts as well as the presence of NaOH are necessary to observe appreciable conversions. The base facilitates the formation of ruthenium alkoxide by abstracting proton of the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. This



Scheme 1. Synthesis of the $[Ru((Ph_2P)_2N{-}C_6H_4$-2-$CH(CH_3)_2)(\eta^6\text{-}p\text{-cymene})Cl]Cl$ (**5**), $[Ru((Ph_2P)_2N{-}C_6H_4$-4-$CH(CH_3)_2)(\eta^6\text{-}p\text{-cymene})Cl]Cl$, (**6**) and $[RuCp^*((Ph_2P)_2N{-}C_6H_4$-4-$CH(CH_3)_2)Cl]$ (**7**) complexes (i) 2 equiv. Ph_2PCl, 2 equiv. Et_3N, thf; (ii) 1 equiv. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$, thf; (iv) 1 equiv. [RuCp*Cl(COD)], thf.

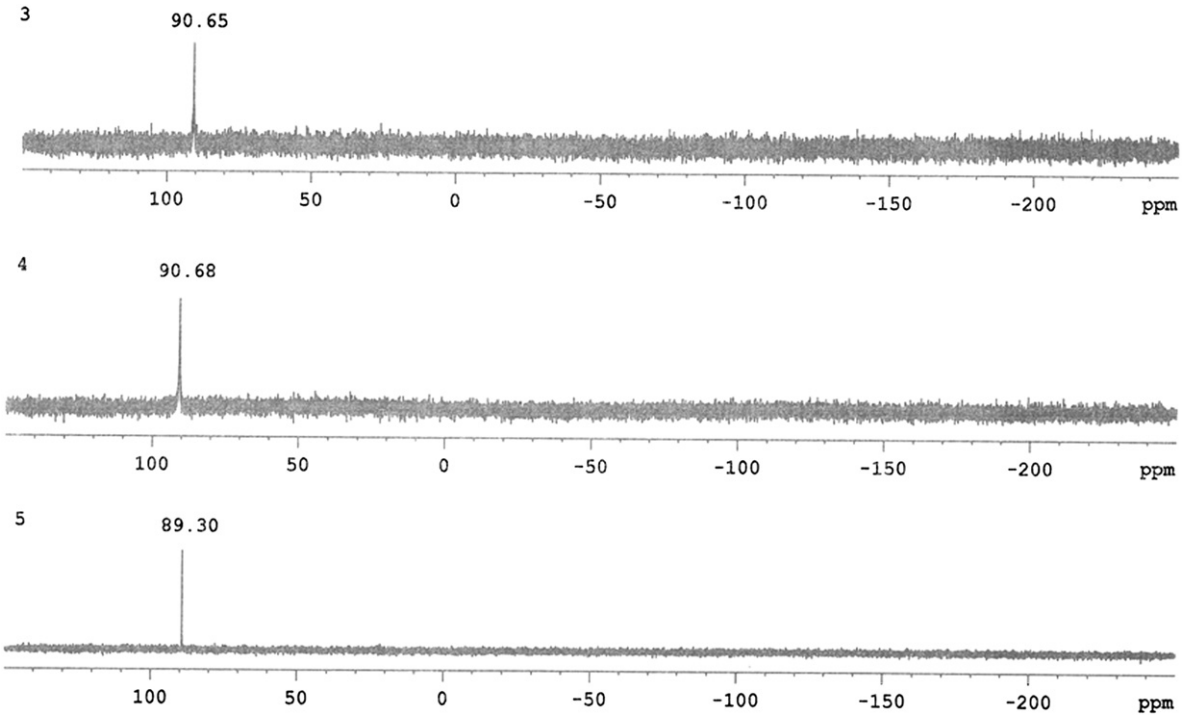
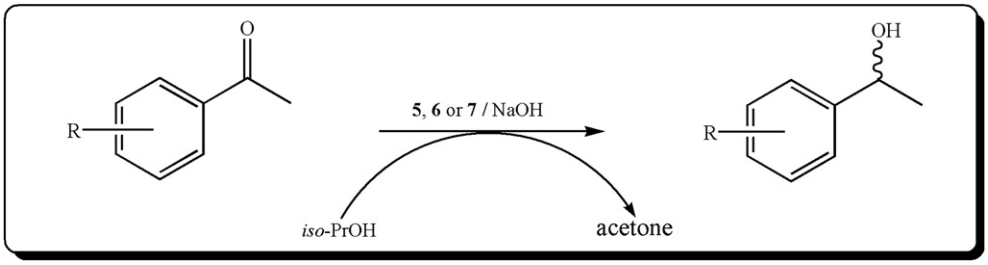


Fig. 1. The $^{31}P-\{^1H\}$ NMR spectra of complexes: (**5**), [Ru((Ph$_2$P)$_2$N-C$_6$H$_4$-2-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl; (**6**), [Ru((Ph$_2$P)$_2$N-C$_6$H$_4$-4-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl; (**7**), [RuCp*((Ph$_2$P)$_2$N-C$_6$H$_4$-4-CH(CH$_3$)$_2$)Cl].

is the mechanism proposed by several research groups on the studies of ruthenium catalyzed transfer hydrogenation reaction by metal hydride intermediates [48–51]. Namely, role of the base is to generate a more nucleophilic alkoxide ion which would rapidly attack the ruthenium complex responsible for dehydrogenation of *iso*-PrOH. As Table 1 shows, high conversions can be achieved with the **5**–**7** catalytic systems. Next, performing the reaction in air or water, slowed down the reaction but did not affect yield of the product. In addition, we have expanded the substrate-to-catalyst ratio to observe the effect on the catalytic efficiency. As shown in Table 1, increasing the substrate-to-catalyst ratio does not damage the conversions of the product in most cases except time of the reaction lengthened. Remarkably, the transfer hydrogenation of acetophenone could be achieved to 99% yield even when the substrate-to-catalyst ratio reached 1000:1. Results obtained from optimization studies indicated clearly that the excellent yields were achieved in the reduction of acetophenone to 1-phenylethanol when **5**, **6** or **7** was used as the catalytic precursor in 15 min, 30 min and 4 h, respectively with a substrate-catalyst molar ratio (100:1) in *iso*-PrOH at 82 °C (Table 1). It should be pointed out that complexes **5**, **6** and **7** are more active catalysts than the corresponding precursor: [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (41% maximum yield in 24 h) with a 1/14 complex/NaOH ratio [52].

The catalytic reduction of acetophenone derivatives was all tested with the conditions optimized for acetophenone. The reactions with the [Ru((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl, **6** or [RuCp*((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)Cl], **7** catalytic system proceeded more slowly than that of [Ru((Ph$_2$P)$_2$N-C$_6$H$_4$-2-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl, **5**. It is noteworthy that the [Ru((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl, **6** or [RuCp*((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)Cl], **7** display the differences in reactivity (Table 1). That's to stay, the catalytic activities in the studied hydrogen transfer reactions were generally much higher for the [Ru((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl, **6** than for the [RuCp*((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)Cl], **7**. For example, under the identical conditions, transfer hydrogenation of acetophenone derivatives with the system **6** led to 92–99% conversions within 30 min whereas with **7**, the same 92–99% conversions were achieved only after 4 h period (Table 2). The encouraging catalytic results obtained with complex **6** catalyst prompted us to investigate and to change the position of the isopropyl group on the aniline. The complex **5** has proved to be excellent catalyst precursor in transfer hydrogenation of acetophenone derivatives, leading to corresponding alcohols in 15 min (up to 93–99% yield). This higher catalytic activity can be explained by the nature of the bis(aminophosphine) ligand which can generate an open coordination site at



Scheme 2. Hydrogen transfer from *iso*-PrOH to acetophenone derivatives.

Table 1
Transfer hydrogenation of acetophenone with *iso*-PrOH catalyzed by [Ru((Ph$_2$P)$_2$N–C$_6$H$_4$-2-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl (**5**), [Ru((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl (**6**) and [RuCp*((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)Cl] (**7**).

Entry	Catalyst	S/C/NaOH	Time	Conversion (%)[h]	TOF(h^{-1})[i]
1	**5**[a]	100:1:5	1 h	<2	–
2	**6**[a]	100:1:5	1 h	<2	–
3	**7**[a]	100:1:5	1 h	<2	–
4	**5**[b]	100:1	1 h	<5	–
5	**6**[b]	100:1	1 h	<5	–
6	**7**[b]	100:1	1 h	<5	–
7	**5**[c]	100:1:5	30 min	98 (96, 93)[k]	196
8	**6**[c]	100:1:5	1.5 h	99 (95, 92)[k]	66
9	**7**[c]	100:1:5	10 h	98 (95, 93)[k]	10
10	**5**[d]	100:1:5	30 min	98	196
11	**6**[d]	100:1:5	1 h	99	99
12	**7**[d]	100:1:5	6 h	97	16
13	**5**[e]	500:1:5	1 h	98	98
14	**6**[e]	500:1:5	12 h	96	8
15	**7**[e]	500:1:5	12 h	97	8
16	**5**[f]	1000:1:5	2.5 h	96	38
17	**6**[f]	1000:1:5	4 h	98	25
18	**7**[f]	1000:1:5	32 h	99	<3
19	**5**[g]	100:1:5	10 min	82	492
20	**6**[g]	100:1:5	10 min	40	240
21	**7**[g]	100:1:5	10 min	6	36

[a] At room temperature; acetophenone/Ru/NaOH, 100:1:5.
[b] Refluxing in *i*PrOH; acetophenone/Ru, 100:1, in the absence of base.
[c] Added 0.1 mL of H_2O.
[d] Refluxing the reaction in air.
[e] Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 500:1:5.
[f] Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 1000:1:5.
[g] Refluxing in *iso*-PrOH; acetophenone/Ru/NaOH, 100:1:5.
[h] Determined by GC (three independent catalytic experiments).
[i] Referred at the reaction time indicated in column; TOF = (mol product/mol Ru(II)Cat.)xh^{-1}.
[k] The amount of the water in different concentrations (0.5, 1.0 mL).

ruthenium more easily. Furthermore, complex **5** showed very high activity for most of the ketones. The introduction of electron withdrawing substituents, such as F, Cl and Br to the *para* position of the aryl ring of the ketone decreased the electron density of the C=O bond so that the activity was improved giving rise to easier hydrogenation [53–55]. The examination of the results indicates clearly that with each of the tested complexes, the best yield was achieved in the reduction of acetophenone derivatives when [Ru((Ph$_2$P)$_2$N-C$_6$H$_4$-2-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl, **5** was used as the catalyst precursor. In order to investigate the evolution of the catalyst, **5**, **6** or **7**, ^{31}P–{^{1}H} NMR spectrum was recorded immediately after the catalytic reaction. The observed singlet at 21.6 ppm in the spectrum corresponds to hydrolysis product diphenylphosphinous acid, Ph$_2$P(O)H [56–58].

Table 2
Transfer hydrogenation results for substituted acetophenones with the Catalyst systems: [Ru((Ph$_2$P)$_2$N-C$_6$H$_4$-2-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl (**5**), [Ru((Ph$_2$P)$_2$N-C$_6$H$_4$-4-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl (**6**) and [RuCp*((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)Cl] (**7**).[a]

Entry	R	Catalyst	Time	Conv.(%)[b]	TOF(h^{-1})[c]
1	**5**	H	15 min	96	384
2		4-F	15 min	99	396
3		4-Cl	15 min	97	388
4		4-Br	15 min	96	384
5		2-MeO	15 min	94	376
6		4-MeO	15 min	93	372
7	**6**	H	30 min	97	194
8		4-F	30 min	99	198
9		4-Cl	30 min	98	196
10		4-Br	30 min	95	190
11		2-MeO	30 min	93	186
12		4-MeO	30 min	92	184
13	**7**	H	4 h	97	24
14		4-F	4 h	99	25
15		4-Cl	4 h	99	25
16		4-Br	4 h	96	24
17		2-MeO	4 h	94	24
18		4-MeO	4 h	92	23

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), NaOH (0.025 mmol), 82 °C, 15 min for **5**, 30 min for **6** and 4 h for **7**, respectively, the concentration of acetophenone derivatives is 0.1 M.
[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.
[c] TOF = (mol product/mol Cat.) × h^{-1}.

3. Conclusion

In conclusion, we synthesized several octahedral Ru(II) complexes of formula [Ru((Ph$_2$P)$_2$N–C$_6$H$_4$-2-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl, [Ru((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl and [RuCp*((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)Cl], which were fully characterized. These compounds have proved to be efficient catalysts in the transfer hydrogenation reaction (HTR) of ketones in basic *iso*-PrOH. Especially, the C$_6$H$_4$-2-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl catalytic system demonstrates remarkable catalytic reactivity and in a certain case, alcohols with up to 99% yield could be obtained even when the substrate-to-catalyst molar ratio reached 1000:1. Furthermore, performing the reaction in air slowed down the reaction, but the conversion was not incredible affected in the air or addition of water. When we increased the amount of water in the reaction system, the high yield remained intact.

4. Experimental

4.1. Materials and methods

Unless otherwise stated, all reactions were carried out under an atmosphere of argon using conventional Schlenk glass-ware, solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. PPh$_2$Cl, 2-isopropylaniline and 4-isopropylaniline are purchased from Fluka and were used as received. [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ [30] and [RuCp*Cl(COD)] [59] were prepared according to literature procedures. The IR spectra were recorded on a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr pellets. ^{1}H (400.1 MHz), ^{13}C NMR (100.6 MHz) and ^{31}P–{^{1}H} NMR spectra (162.0 MHz) were recorded on a Bruker Avance 400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4 respectively. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded by Gallenkamp Model apparatus with open capillaries.

4.2. GC analyses

GC analyses were performed on an HP 6890N Gas Chromatograph equipped with capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m × 0.32 mm × 0.25 μm). The GC parameters were for transfer hydrogenation of ketones as follows; initial temperature, 110 °C; initial time, 1 min; solvent delay, 4.48 min; temperature ramp 80 °C/min; final temperature, 200 °C; final time, 21.13 min; injector port temperature, 200 °C; detector temperature, 200 °C, injection volume, 2.0 μL.

4.3. General procedure for the transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen transfer reaction: a solution of ruthenium complexes [Ru((Ph$_2$P)$_2$N-C$_6$H$_4$-2-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl (**5**), [Ru((Ph$_2$P)$_2$N-C$_6$H$_4$-4-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl, (**6**) or [RuCp*((Ph$_2$P)$_2$N-C$_6$H$_4$-4-CH(CH$_3$)$_2$)Cl] (**7**),

NaOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed *iso*-PrOH (5 mL) were refluxed for 15 min for **5**, 30 min for **6** and 4 h for **7**. After this period a sample of the reaction mixture was taken off, diluted with acetone and analyzed immediately by GC. Conversions obtained are related to the residual unreacted ketone.

4.4. Synthesis of ruthenium complexes

4.4.1. Synthesis of [Ru((Ph$_2$P)$_2$N-C$_6$H$_4$-2-CH(CH$_3$)$_2$)(η^6-p-cymene)ClJCl, (**5**)

To a solution of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (432 mg, 0.685 mmol) in 10 mL thf, a solution (thf, 15 mL) of **3** (356 mg, 0.685 mmol) was added. The resulting reaction mixture was allowed to proceed under stirring at room temperature for 1 h. After this time, the solution was filtered off and the solvent evaporated under vacuum, the solid residue thus obtained was washed with diethyl ether (3 × 15 mL) and then dried under vacuum (Scheme 1). Following recrystalization from diethylether/CH_2Cl_2, a red crystalline powder was obtained (yield 510 mg, 89.2%), m.p. 284–285 °C ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 6.89–7.56 (m, 20H, *o, m, p*-hydrogens of phenyls and 4H, aromatic hydrogens of aniline), 5.45 (d, 2H, ^3J = 5.20 Hz, aromatic hydrogens of *p*-cymene), 5.26 (d, 2H, ^3J = 5.20 Hz, aromatic hydrogens of *p*-cymene), 2.96 (br, 1H, –C**H**(CH$_3$)$_2$– of aniline), 2.85 (m, 1H, –C**H**– of *p*-cymene), 2.10 (s, 3H, C**H**$_3$-Ph of *p*-cymene), 1.22 (d, 6H, ^3J = 6.4 Hz, (C**H**$_3$)$_2$CHPh of *p*-cymene); 0.33 (br, –CH(C**H**$_3$)$_2$– of aniline), ppm; ^{13}C–{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 145.25 (**C**-1), 140.32 (**C**-2), 138.21 (*i*-carbons of phenyls), 135.21 (*o*-carbons of phenyls), 132.00 (s, *p*-carbons of phenyls), 130.17 (**C**-4), 129.04 (**C**-3), 127.79 (**C**-5), 127.26 (*m*-carbons of phenyls), 125.69 (**C**-6), 77.78, 79.28 (aromatic carbons of *p*-cymene), 96.36, 99.94 (quaternary carbons of *p*-cymene), 31.09 (–**C**H– of *p*-cymene), 27.27 (–**C**H(CH$_3$)$_2$– of aniline), 23.31 (–CH(**C**H$_3$)$_2$– of aniline), 22.26 ((**C**H$_3$)$_2$CHPh of *p*-cymene), 18.94 (**C**H$_3$Ph of *p*-cymene), ppm: assignment was based on the ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 90.71 (s); IR, (KBr): υ = 945 (P–N–P), 1441 (P-Ph) cm^{-1}; $C_{43}H_{45}NP_2RuCl_2$ (809.8 g/mol): calcd. C 63.78, H 5.60, N 1.73; found C 63.61, H 5.52, N 1.69.

4.4.2. Synthesis of [Ru((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)(η^6-p-cymene)ClJCl, (**6**)

To a solution of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (421 mg, 0.689 mmol) in 10 mL thf, a solution (thf, 15 mL) of **4** (346 mg, 0.689 mmol) was added. The resulting reaction mixture was allowed to proceed under stirring at room temperature for 2 h. After this time, the solution was filtered off and the solvent evaporated under vacuum, the solid residue thus obtained was washed with diethyl ether (3 × 15 mL) and then dried under vacuum (Scheme 1). Following recrystalization from diethylether/CH_2Cl_2, a red crystalline powder was obtained (yield 520 mg, 93.5%), m.p. 250 °C (dec.). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.29–7.69 (m, 20H, *o, m and p*-hydrogens of phenyls), 6.80 (d, 2H, J_{H-H} = 7.6 Hz, **H**-3 and H-**5**), 6.63 (d, 2H, J_{H-H} = 8.0 Hz, **H**-2 and **H**-6), 5.52 (d, 2H, ^3J = 5.20 Hz, aromatic hydrogens of *p*-cymene), 5.38 (d, 2H, ^3J = 5.20 Hz, aromatic hydrogens of *p*-cymene), 2.82 (m, 1H, –C**H**– of *p*-cymene), 2.71 (m, 1H, –C**H**(CH$_3$)$_2$– of aniline), 2.27 (s, 3H, C**H**$_3$-Ph of *p*-cymene), 1.26 (d, 6H, ^3J = 6.60 Hz, (C**H**$_3$)$_2$CHPh of *p*-cymene), 1.14 (d, 6H, J_{H-H} = 6.80 Hz, –CH(C**H**$_3$)$_2$– of aniline) ppm; ^{13}C–{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 144.55 (**C**-1), 141.60 (**C**-4), 134.20 (*i*-carbons of phenyls), 132.44 (*o*-carbons of phenyls), 132.42 (*p*-carbons of phenyls), 127.55 (*m*-carbons of phenyls), 126.82 (**C**-3 and **C**-5), 123.64 (**C**-2 and **C**-6), 78.20, 79.85 (aromatic carbons of *p*-cymene), 95.42, 100.40 (quaternary carbons of *p*-cymene), 33.16 (–**C**H(CH$_3$)$_2$– of aniline), 31.05 (–**C**H– of *p*-cymene), 23.81 (–CH(**C**H$_3$)$_2$– of aniline), 22.30 ((**C**H$_3$)$_2$CHPh of *p*-cymene), 18.96 (**C**H$_3$Ph of *p*-cymene), ppm: assignment was based on the ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 86.51 (s); IR, (KBr): υ = 937 (P–N–P), 1441 (P-Ph) cm^{-1}; $C_{43}H_{45}NP_2RuCl_2$ (809.8 g/mol): calcd. C 63.78, H 5.60, N 1.73; found C 63.58, H 5.56, N 1.68.

4.4.3. Synthesis of [RuCp*((Ph$_2$P)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)Cl] (**7**)

To a solution of [RuCp*Cl(COD)] (267 mg, 0.689 mmol) in 10 mL thf, a solution (thf, 15 mL) of **4** (346 mg, 0.689 mmol) was added. The resulting reaction mixture was allowed to proceed under stirring at room temperature for 3 h. After this time, the solution was filtered off and the solvent evaporated under vacuum, the solid residue thus obtained was washed with diethyl ether (3 × 15 mL) and then dried under vacuum (Scheme 1). Following recrystalization from diethylether/CH_2Cl_2, a brick red crystalline was obtained (yield 380 mg, 92.3%), m.p. 233–235 °C ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.13–7.47 (m, 20H, *o, m and p*-hydrogens of phenyls), 6.71 (d, 2H, J_{H-H} = 7.60 Hz, **H**-3 and H-**5**), 6.46 (d, 2H, J_{H-H} = 8.40 Hz, **H**-2 and **H**-6), 2.65 (m, 1H, –C**H**(CH$_3$)$_2$– of aniline), 1.42 (s, 15H, hydrogens of Cp*), 1.04 (d, 6H, J_{H-H} = 6.80 Hz, –CH(C**H**$_3$)$_2$– of aniline) ppm; ^{13}C–{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 143.25 (**C**-1), 138.23 (**C**-4), 134.28 (*i*-carbons of phenyls), 132.18 (*o*-carbons of phenyls), 129.64 (*p*-carbons of phenyls), 127.75 (*m*-carbons of phenyls), 126.08 (**C**-3 and **C**-5), 126.99 (**C**-2 and **C**-6), 90.12 (carbons Cp*), 33.33 (–**C**H(CH$_3$)$_2$– of aniline), 23.87 (–CH(**C**H$_3$)$_2$– of aniline), 9.79 (carbons **C**H$_3$-Cp*), ppm: assignment was based on the ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 89.28 (s); IR, (KBr): υ = 938 (P–N–P), 1435 (P-Ph) cm^{-1}; $C_{43}H_{46}NP_2RuCl$ (775.3 g/mol): calcd. C 66.62, H 5.98, N 1.81; found C 66.48, H 5.93, N 1.78.

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