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New active ruthenium(II) complexes based N3,N3′-bis(diphenylphosphino)-2,2′-bipyridine-3,3′-diamine and P,P′-diphenylphosphinous acid-P,P′-[2,2′-bipyridine]-3,3′-diyl ester ligands for transfer hydrogenation of aromatic ketones by propan-2-ol

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ABSTRACT

The dimeric starting material $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ reacts with N3,N3′-bis(diphenylphosphino)-2,2′-bipyridine-3,3′-diamine, **1** and P,P′-diphenylphosphinous acid-P,P′-[2,2′-bipyridine]-3,3′-diyl ester, **2** ligands to afford bridged dinuclear complexes $[C_{10}H_6N_2\{NHPPh_2\text{-}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **3** and $[C_{10}H_6N_2\{OPPh_2\text{-}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **4** in quantitative yields. These bis(aminophosphine) and bis(phosphinite) based Ru(II) complexes serve as active catalyst precursors for the transfer hydrogenation of acetophenone derivatives in 2-propanol and especially **4** acts as a good catalyst, giving the corresponding alcohols in 99% yield in 20 min (TOF $\leqslant 280\ h^{-1}$).

1. Introduction

Transition metal-catalyzed procedures for transfer hydrogenation of a wide variety of functional groups by different hydrogen donors are an interesting alternative to conventional hydrogenation [1,2]. Ketones are the most common unsaturated substrates used in organic synthesis. Extensive efforts have been devoted to their reduction into secondary alcohols especially via hydrogenation [3]. Transfer hydrogenation of ketones by propan-2-ol is convenient in large-scale synthesis since there is no need to employ a high hydrogen pressure or to use hazardous reducing agents [4]. In addition, the enantioselective hydrogenation of prochiral ketones, which is one of the most exciting and powerful method of synthesing chiral alcohols, has been receiving increased attention as well and has led to notable success [5]. Although very frequently ruthenium-based catalysts have been applied in the enantioselective hydrogenation of prochiral ketones [6], rhodium complexes have proven to lead very efficient processes along with potential industrial applications [7–9].

Three decades ago, it has been shown by Schrock and Osborn that the use of rather basic alkyl phosphines allowed the hydrogenation of simple ketones in the presence of rhodium catalysts [10]. Electron rich phosphines are now recognized to greatly enhance the rate of ketone hydrogenation by rhodium complexes [11,12].

The chemistry of aminophosphines and phosphinites has been intensively explored in recent years [13]. These compounds are extremely attractive as potential ligands since various structural modifications are accessible via simple P–N and P–O bond formation [14]. Many modified phosphine ligands and a variety of chiral aminophosphine–phosphinite ligands have important applications in organomatallic chemistry and catalysis, giving selective catalysts for hydroformylation, hydrosilylation and asymmetric transfer hydrogenation [15,16]. While much effort has been devoted to the synthesis of aminophosphines and their metal complexes, similar studies on the analogous bis(phosphinites) are less extensive [17], even though some of their complexes has proved to be efficient catalysts [18].

We previously reported the preparation of the N3,N3′-bis(diphenylphosphino)-2,2′-bipyridine-3,3′-diamine and P,P′-diphenylphosphinous acid-P,P′-[2,2′-bipyridine]-3,3′-diyl ester and their chalcogenides [19]. As a part of our interest in designing new ligand systems with different spacers to control the electronic attributes at phosphorus centers and to explore their coordination chemistry, we report here the synthesis of bridged dinuclear Ru(II) complexes $[C_{10}H_6N_2\{NHPPh_2\text{-}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **3** and $[C_{10}H_6N_2\{OPPh_2\text{-}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **4** and their catalytic evaluation in the transfer hydrogenation of ketones.

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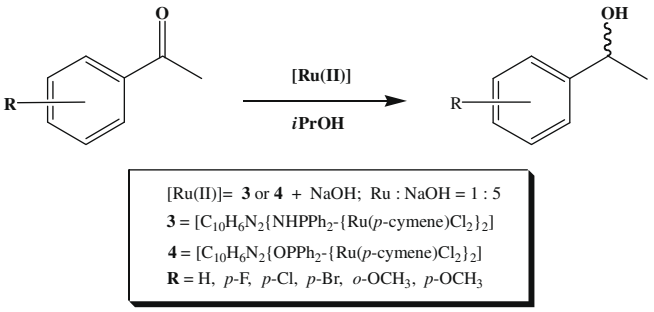
2. Results and discussion

Synthesis and characterization of bis(aminophosphine), **1** and bis(phosphinite), **2** ligands with rigid backbones, prepared from the starting materials 3,3′-diamino-2,2′-bipyridine and 3,3′-dihydroxy-2,2′-bipyridine by the aminolysis and hydrolysis methods, respectively, were previously reported [19] (Scheme 1).

The reaction of stoichiometric amounts of $[Ru(p\text{-cymene})Cl_2]_2$ and $[(Ph_2PNH)_2\text{-}C_{10}H_6N_2]$, **1** affords complex $[C_{10}H_6N_2\{NHPPh_2\text{-}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **(3)** in high yield as a red microcrystalline powder, this compound being stable in air. Complex **1** was expected to cleave the $[Ru(p\text{-cymene})Cl_2]_2$ dimer to give the corresponding complex **3** via monohapto coordination of the aminophosphine group. Analysis by $^{31}P\text{–}\{^1H\}$ NMR exhibits a unique signal in the spectrum, indicative of both phosphorus being equivalent as a result of the high symmetry of the complex. The $^{31}P\text{–}\{^1H\}$ NMR spectrum of **3** shows a single resonance at 52.00 ppm, in line with the values previously observed for similar compounds [20]. Analysis by ^1H NMR reveals this compound to be diamagnetic, exhibiting signals corresponding to the aromatic rings for **3** at 8.04–7.41 ppm. Another set of signals consisting of two doublets centered at 5.20 and 5.11 ppm are due to the presence of the aromatic protons in the *p*-cymene group, this information is complemented by the presence of signals at 2.66 and 0.90 ppm due to the CH and CH_3 of the *iso*-propyl groups of the *p*-cymene moiety. Finally, a signal due to the presence of the methyl in the *p*-cymene group is observed at 1.73 ppm. Furthermore in the $^{13}C\text{–}\{^1H\}$ NMR spectrum of **3**, $J(^{31}P\text{–}^{13}C)$ coupling constants of the carbons of the phenyl rings was observed, which is consistent with the literature values [21]. The structures of the **3** was further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values.

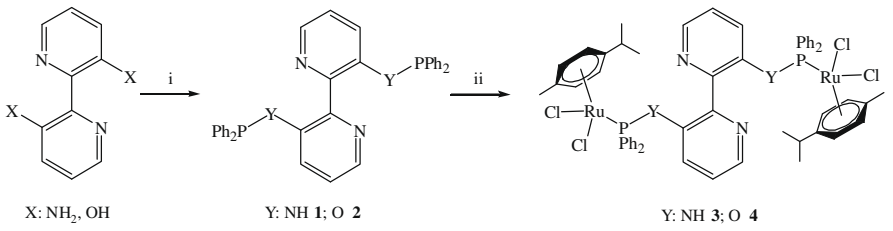
We also examined simple coordination chemistry of **2** with $[Ru(p\text{-cymene})Cl_2]_2$. Complexation reaction was straightforward, with coordination to ruthenium being carried out at room temperature. The reaction of $[Ru(p\text{-cymene})Cl_2]_2$ with one equivalent of $[(Ph_2PO)_2\text{-}C_{10}H_6N_2]$, **2** affords the corresponding monodendate $[C_{10}H_6N_2\{OPPh_2\text{-}Ru(\eta^6\text{-p-cymene})Cl_2\}_2]$ **4**, in high yield as the main product. The initial color change, i.e., from clear orange to deep red [22], attributed to the dimer cleavage most probably by the bis(phosphinite) ligand. The $^{31}P\text{–}\{^1H\}$ NMR spectrum is quite consistent with the structure [23], that of contain **4** shows single resonance at δ 119.09 ppm. To the best of our knowledge Ceron-Camacho and co-workers [24] have been reported the first crystallographic determination of a bimetallic bridged structure using this sort of ligands. Furthermore, a related structure has been invoked by Balakrishna and co-workers [25] for the formation of the ruthenium complex where the ligands also serves as bridge between two metal centers, however no crystallographic evidence was presented. Most recently [26] a similar structure has been determined for a BINAP-based phosphinite ligand BINAPO, where as is the case for complex **4**, it is noted by the authors that compounds bearing binaphtyl-based ligands bridging two metal centers are very rare. In the ^{13}C NMR spectrum through-space P–C coupling was observed. Furthermore, ^1H NMR spectral data of **4** is consistent with the structure proposed. In the ^1H NMR spectrum, **4** is characterized by isopropyl methyl doublets, at δ 0.88 ppm and η^6-arene doublets at δ 5.59 and 5.35 ppm. The structural composition of the complex has been confirmed by IR and elemental analysis. Although, single crystals of **3** and **4** were obtained by slow diffusion of diethylether into a solution of the compound in dichloromethane over several days, unfortunately we were not able to protect the crystals from rapid decomposition in air.



Scheme 2. Hydrogen transfer from *i*PrOH to acetophenone derivatives.

The excellent catalytic performance of phosphinite- and aminophosphine-based transition metal complexes [27] prompted us to develop new Ru(II) complexes with well-shaped ligands. To this end, we examined the catalytic activation of complexes **3** and **4** in the transfer hydrogenation of aryl ketones to the corresponding alcohols (Scheme 2).

Complexes **3** and **4** were used as precatalysts, *i*PrOH/NaOH as the reducing system, and acetophenone as the model substrate. 2-Propanol is the conventional hydrogen source having favorable properties; it is stable, easy to handle (b.p. 82 °C), non-toxic, environmentally friendly, inexpensive and dissolves in many organic compounds. Moreover, the acetone product is readily removable [28]. The catalytic activities of complexes **3** and **4** were not deeply investigated, because of their instability in solutions. All the catalytic reactions were interrupted after 10, 20, 30 and 60 min. The catalytic results are collected in Table 1. At room temperature no appreciable formation of 1-phenylethanol was observed (Table 1, Entries 1 and 2) 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. However, when the temperature was increased to 82 °C smooth reduction of acetophenone into 1-phenylethanol occured, with conversion ranging from 92% to 99% after 1 h for **3** and 20 min for **4** of reaction. The catalytic activities of **3** and **4** are comparable, with the values referred to 10 min of 135 and 275.4 h^{-1}, respectively (Table 1, Entries 3 and 4). These values correspond to 22.5% and 45.9% conversions, respectively. As can be inferred from the Table 2 (Entries 5 and 6) the precatalysts as well as the presence of NaOH are necessary to observe appreciable conver-



Scheme 1. Synthesis of the $[C_{10}H_6N_2\{NHPPh_2\text{-}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **3** and $[C_{10}H_6N_2\{OPPh_2\text{-}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **4** complexes (i) 2 equiv. Ph_2PCl, 2 equiv. Et_3N, CH_2Cl_2 for **1** and toluene for **2** and (ii) 1 equiv. $[Ru(p\text{-cymene})Cl_2]_2$, thf.

Table 1
Transfer hydrogenation of acetophenone catalyzed by **3** and **4**.

Entry	Complex	Time (min)	Conversion (%)[e]	TOF (h^{-1})[f]
1	**3**[a]	30	<1	
2	**4**[a]	30	<1	
3	**3**[b]	10	22.5	135
4	**4**[b]	10	45.9	275.4
5	**3**[b]	20	42.5	127.5
6	**4**[b]	20	99.0	297.0
7	**3**[b]	60	95.2	95.2
8	**3**[c]	60		
9	**4**[c]	60		
10	**3**[d]	10	3.2	192
11	**4**[d]	10	6.5	390

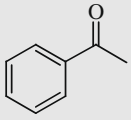
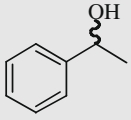
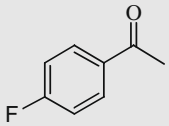
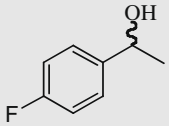
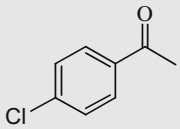
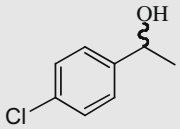
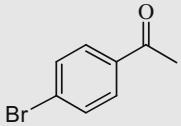
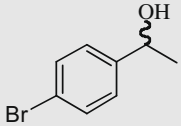
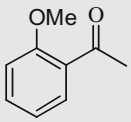
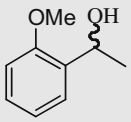
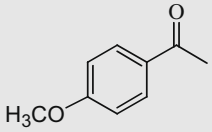
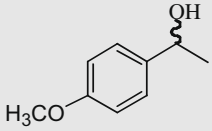
[a] *Reaction conditions*: at room temperature. acetophenone/Ru/NaOH, 100:1:5.
[b] *Reaction conditions*: refluxing in *i*PrOH; acetophenone/Ru/NaOH, 100:1:5.
[c] In the absence of base.
[d] *Reaction conditions*: refluxing in *i*PrOH; acetophenone/Ru/NaOH, 1000:1:5.
[e] Determined by GC (three independent catalytic experiments).
[f] Referred at the reaction time indicated in column; TOF = (mol product/mol Ru(II) Cat.) × h^{-1}.

sions. 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 is the mechanism proposed by several workers on the studies of ruthenium catalyzed transfer hydrogenation reaction by metal hydride intermediates [29,30].

Results obtained from optimization studies indicate clearly that the excellent yields were achieved in the reduction of acetophenone to 1-phenylethanol when **3** and **4** were used as the catalytic precursor in 60 min and 20 min, respectively, with a substrate–catalyst molar ratio (100:1) in 2-propanol containing a small amount of NaOH at 82 °C (Table 1). The catalytic reduction of acetophenone derivatives were all tested with the conditions optimized for acetophenone. The reaction with the bis(aminophosphine)-Ru(II), **3** catalytic system proceeded more slowly than bis(phosphinite)-Ru(II), **4**. But ruthenium(II) complex with bis(aminophosphine) ligand also gave the same yields in 1 hour. It thus appears that the nature of the bis(phosphinite) and bis(aminophosphine) ligand can also play a crucial role in the transfer hydrogenation reactions. These results indicate that the O–P and NH–P linkages possibly can stabilize a catalytic transition state [31].

Complexes **3** and **4** showed very good 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 [32].

Table 2
Transfer hydrogenation of substituted acetophenones catalyzed by $[C_{10}H_6N_2\{NHPPh_2\text{-}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **3** and $[C_{10}H_6N_2\{OPPh_2\text{-}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **4**.

Entry	Substrate	Product	Catalyst	Yield (%)[a,b]	TOF (h^{-1})[c]
1			**3**	95.2	95.2
2			**4**	99.0	297.0
3			**3**	98.3	98.3
4			**4**	99.1	297.3
5			**3**	96.5	96.5
6			**4**	95.1	285.3
7			**3**	97.9	97.9
8			**4**	98.0	294.0
9			**3**	96.4	96.4
10			**4**	98.9	296.7
11			**3**	92.5	92.5
12			**4**	93.7	281.1

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *i*PrOH (5 mL), NaOH (0.025 mmol), 82 °C, 1.0 h for **3** and 1/3 h for **4**.
[b] Purity of compounds is checked by NMR and GC, yields are based on methyl aryl ketone.
[c] TOF = (mol product/mol Cat.) × h^{-1}.

3. Conclusions

In summary, we have synthesized and characterized two new bimetallic Ru(II) complexes based bis(aminophosphine) and bis(phosphinite) monodendate ligands and investigated their use in transfer hydrogenation of ketones. We have found that these complexes are efficient homogeneous catalytic systems that can be readily implemented and lead to secondary alcohols from good to excellent yields. The catalytic activities in the studied hydrogen transfer reactions were generally much higher for the bis(phosphinite) ligand than those for the bis(aminophosphine) ligand. This higher catalytic activity can be explained by the inherent hemilabile character of the phosphinite ligand which can generate an open coordination site at ruthenium more easily, thus allowing a faster substrate complexation. The procedure is simple and efficient towards various aryl ketones. Future investigations are aiming at the development of an asymmetric version of this process.

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_2Cl, 2-chloro-3-nitropyridine and 2-bromo-3-hydroxypyridine are purchased from Fluka and were used as received. The starting materials 3,3′-diamino-2,2′-bipyridine [33], 3,3′-dihidroxy-2,2′-bipyridine [34], [Ru(*p*-cymene)Cl_2]$_2$ [35], 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 spectra on a Bruker Avance 400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4, respectively. GC analyses were performed on a HP 6890N Gas Chromatograph equipped with capillary column (%5 biphenyl, %95 dimethylsiloxane) (30 m × 0.32 mm × 0.25 μm). Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument; melting points by Gallenkamp Model apparatus with open capillaries.

4.2. Synthesis of [$C_{10}H_6N_2${$NHPPh_2$-Ru(η^6-*p*-cymene)Cl_2}$_2$], **3**

To a solution of [(η^6-*p*-cymene)$RuCl_2$]$_2$ (55 mg, 0.09 mmol) in CH_2Cl_2, a solution (CH_2Cl_2, 30 mL) of $(Ph_2PNH)_2$-$C_{10}H_6N_2$, **1** (50 mg, 0.09 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 × 10 mL) and then dried under vacuum (Scheme 1). Following recrystallization from diethylether/CH_2Cl_2, a red powder was obtained (yield 94 mg, 89.4%), m.p. > 200 °C (dec.). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 12.25 (d, 2H, $^3J_{NHP}$ = 10.80 Hz, N***H***-P), 8.06 (d, 2H, *J* = 3.60, H-6), 8.04 (dd, 8H, *J* = 6.30 and 11.40 Hz, *o*-protons of phenyls), 7.41 (m, 12H, *m*- and *p*-protons of phenyls), 7.20 (d, 2H, *J* = 8.40, H-4), 6.86 (dd, 2H, *J* = 4.26 and 9.20, H-5), 5.20 (d, 4H, *J* = 5.60 Hz, aromatic hydrogen of *p*-cymene), 5.11 (d, 4H, *J* = 5.20 Hz, aromatic hydrogen of *p*-cymene), 2.66 (m, 2H, –C***H***– of *p*-cymene), 1.73 (s, 6H, C***H***$_3$-Ph of *p*-cymene), 0.90 (d, 12H, *J* = 6.60 Hz, (C***H***$_3$)$_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.48 (***C***H$_3$Ph of *p*-cymene), 21.47 ((***C***H$_3$)$_2$CHPh of *p*-cymene), 30.21 (–***C***H– of *p*-cymene), 86.95, 90.30 (CH$_3$-C***C***H$_2$***C***H$_2$C-CH(CH$_3$)$_2$ of *p*-cymene), 122.50 (C-5), 127.20 (C-4), 128.15 (d, *J* = 10.06 Hz, *m*-carbons of phenyls), 130.62 (s, *p*-carbons of phenyls), 132.37 (d, *J* = 9.05 Hz, *o*-carbons of phenyls), 134.90 (d, *J* = 34.00 Hz, *i*-carbons of phenyls), 95.41 (CH$_3$-***C***CH$_2$CH$_2$C-CH(CH$_3$)$_2$ of *p*-cymene), 138.05 (C-6), 142.30 (C-3), 110.60 (CH$_3$-CCH$_2$CH$_2$***C***-CH(CH$_3$)$_2$ of *p*-cymene), 148.80 (C-2); assignment was based on the ^{1}H-^{13}C HETCOR spectrum; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 51.94 (s); IR, (KBr): υ = 925 (P–NH), 1439 (P–Ph), 1587 (C=N), 3363 (N–H) cm^{-1}; Anal. Calc. for $C_{54}H_{56}N_4P_2Ru_2Cl_4$: C, 55.58; H, 4.84; N, 4.80. Found: C, 55.46; H, 4.81; N, 4.75%.

4.3. Synthesis of [$C_{10}H_6N_2${$OPPh_2$-Ru(η^6-*p*-cymene)Cl_2}$_2$], **4**

To a solution of [(η^6-*p*-cymene)$RuCl_2$]$_2$ (55 mg, 0.09 mmol) in thf, a solution (thf, 10 mL) of $(Ph_2PO)_2$-$C_{10}H_6N_2$, **2** (50 mg, 0.09 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 × 10 mL) and then dried under vacuum (Scheme 1). Following recrystallization from diethylether/CH_2Cl_2, a red powder was obtained (yield 96 mg, 91.4%), m.p. 143–145 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 8.67 (d, 2H, *J* = 4.40, H-6), 7.98 (d, 2H, *J* = 8.40, H-4), 7.22–7.62 (m, 20H, *o*-, *m*- and *p*-protons of phenyls), 6.91 (dd, 2H, *J* = 4.42 and 8.60, H-5), 5.59 (d, 4H, *J* = 6.00 Hz, aromatic hydrogen of *p*-cymene), 5.35 (d, 4H, *J* = 6.00 Hz, aromatic hydrogen of *p*-cymene), 2.46 (m, 2H, –C***H***– of *p*-cymene), 1.69 (s, 6H, C***H***$_3$-Ph of *p*-cymene), 0.88 (d, 12H, *J* = 6.40 Hz, (C***H***$_3$)$_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.04 (***C***H$_3$Ph of *p*-cymene), 21.61 ((***C***H$_3$)$_2$CHPh of *p*-cymene), 30.00 (–***C***H– of *p*-cymene), 80.50, 85.22 (CH$_3$-C***C***H$_2$***C***H$_2$C-CH(CH$_3$)$_2$ of *p*-cymene), 122.50 (C-5), 128.04 (d, *J* = 10.03 Hz, *m*-carbons of phenyls), 129.03 (C-4), 130.80 (s, *p*-carbons of phenyls), 132.73 (d, *J* = 9.03 Hz, *o*-carbons of phenyls), 136.00 (d, *J* = 40.50 Hz, *i*-carbons of phenyls), 96.70 (CH$_3$-***C***CH$_2$CH$_2$C-CH(CH$_3$)$_2$ of *p*-cymene), 141.80 (C-2), 144.21 (C-6), 110.71 (CH$_3$-CCH$_2$CH$_2$***C***-CH(CH$_3$)$_2$ of *p*-cymene), 148.47 (C-3); assignment was based on the ^{1}H-^{13}C HETCOR spectrum; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 119.09 (s); IR, (KBr): υ = 893 (P–O), 1439 (P–Ph), 1580 (C=N) cm^{-1}. Anal. Calc. for $C_{54}H_{54}N_2O_2P_2Ru_2Cl_4$: C, 55.49; H, 4.66; N, 2.40. Found: C, 55.41; H, 4.59; N, 2.36%.

4.4. Transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen transfer reaction: a suspension of ruthenium complexes [$C_{10}H_6N_2${$NHPPh_2$-Ru(η^6-*p*-cymene)Cl_2}$_2$], **3** (0.005 mmol) or [$C_{10}H_6N_2${$OPPh_2$-Ru(η^6-*p*-cymene)Cl_2}$_2$], **4** (0.005 mmol), NaOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed iso-propanol (5 mL) was refluxed for 60 min for **3** and 20 min for **4**. After this time a sample of the reaction mixture is taken off, diluted with acetone and analyzed by GC, yields obtained are related to the residual unreacted ketone.

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