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Ruthenium-catalyzed transfer hydrogenation of aromatic ketones with aminophosphine or bis(phosphino)amine ligands derived from isopropyl substituted anilines

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ABSTRACT

A series of new highly active Ru(II) complexes with two new (*N*-diphenylphosphino)isopropylanilines, having an isopropyl substituent at carbon 2- (**1**) or 2,6- (**2**) and two new bis(diphenylphosphino)isopropylanilines, having an isopropyl substituent at carbon atom 2- (**3**) or 4- (**4**), were prepared starting from the dimeric complex $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$. All the compounds have been fully characterized by microanalysis, IR, $^{31}P\{1H\}$ NMR, ^{1}H NMR and ^{13}C NMR spectroscopies. Following activation by NaOH, complexes **5**–**8** were tested in the transfer hydrogenation of acetophenone derivatives with *iso*-PrOH as the hydrogen source. Catalytic studies showed that the complexes are excellent catalytic precursors for the transfer hydrogenation of acetophenone derivatives.

1. Introduction

The chemistry of compounds containing phosphorus and nitrogen, with direct bonds between the two elements, has been known for many years, but continues to attract considerable attention, with applications in increasingly diverse fields [1,2]. Potentially this ligand family is extremely attractive since preparative routes enable access to various structural modifications via simple P–N bond formation [3]. Aminophosphines and bis(phosphine)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 to changes in the P–N–P angle and the conformation around the P-centres [4,5]. Small variations in these ligands can cause significant changes in their coordination behaviour and the structural features of the resulting complexes [6].

There has been recently an increasing interest in the synthesis of new and highly active transition-metal based catalysts derived from aminophosphines that can be used in different catalytic reactions including allylic alkylation [7,8], amination [9,10], Heck [11–13], Suzuki [14–16], hydroformylation [17,18], Sonogashira [19], polymerization [20] and hydrogenation reactions [21,22]. Some aminophosphines and derivatives have also found application as anticancer drugs [23], herbicides and antimicrobial agents, as well as neuroactive agents [24].

Organic synthesis needs economically and technically more benign methods that are very general. From an industrial point of view, catalytic transfer hydrogenation is an attractive alternative for high-pressure catalytic hydrogenation with molecular hydrogen [25]. Transition metal catalyzed transfer hydrogenation with 2-propanol is a convenient method to reduce ketones since there is no need for high hydrogen pressure or hazardous reducing agents [26,27]. Homogeneous ruthenium complexes are considered to be the most attractive catalysts for transfer hydrogenation reactions, though other metal complexes have also been used successfully [28,29]. Varying levels of efficiency were observed for ruthenium complexes with ligands such as diamines [30], amino alcohols [31,32], phosphanes [33] and aminophosphines [34].

In the present report, from readily available starting materials, such as isopropyl substituted anilines, two Ru(II)–aminophosphine and two Ru(II)-bis(phosphino)amine complexes have been prepared and characterized. As a part of our interest in designing new ligand systems with different spacers to control the electronic attributes at the phosphorus centers and to explore their coordination chemistry, we report here the synthesis of the Ru(II) complexes $[Ru(\eta^6\text{-}p\text{-cymene})(PPh_2NH\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2)Cl_2]$ (**5**), $[Ru(\eta^6\text{-}p\text{-cymene})(PPh_2NH\text{–}C_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)Cl_2]$ (**6**), $[Ru((PPh_2)_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2)_2Cl_2]$ (**7**) and $[Ru((PPh_2)_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2)_2Cl_2]$ (**8**), and these complexes were also evaluated in the ruthenium-catalyzed transfer hydrogenation of acetophenone derivatives.

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2. Results and discussion

2.1. Synthesis and characterization of the Ru(II) complexes

Following our previous studies [35,36], we prepared a series of ruthenium complexes **5**–**8** from the reaction of $[RuCl(\mu\text{-}Cl)(p\text{-cymene})]_2$ with the monodendate **1**, **2** and chelate ligands **3**, **4** as shown in Scheme 1.

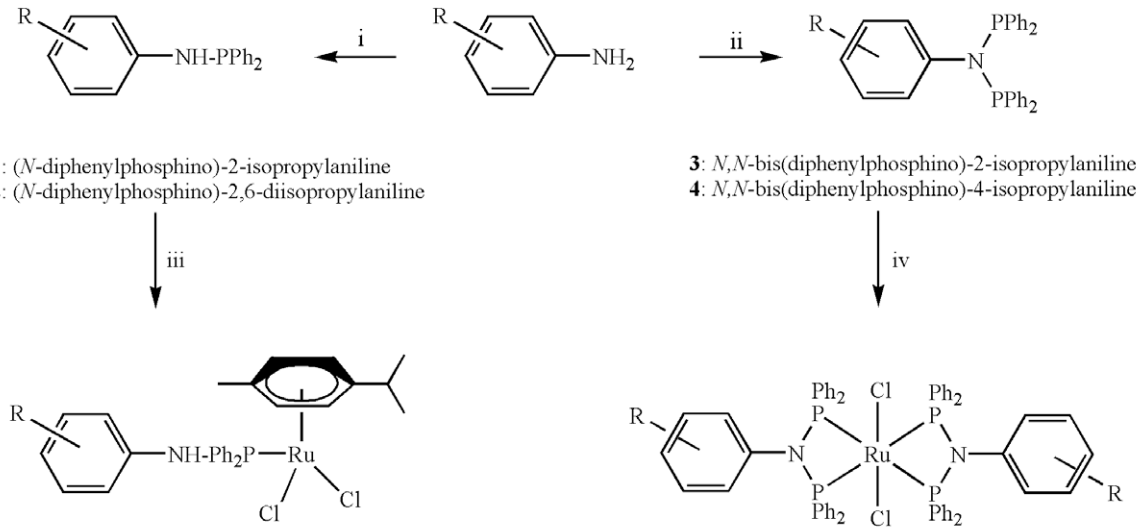
(*N*-diphenylphosphino)isopropylanilines, having an isopropyl substituent at carbon 2- (**1**) or 2,6- (**2**), were easily prepared from the aminolysis of $H_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2$ or $H_2N\text{–}C_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2$, respectively, with one equivalent of chlorodiphenylphosphine in the presence of triethylamine at 0 °C, using thf/CH_2Cl_2 (1/2) and CH_2Cl_2 as the solvent, respectively [37]. The reactions of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ with $PPh_2NH\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2$, **1** and $PPh_2NH\text{–}C_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2$, **2** in CH_2Cl_2 in a ratio of 1/2:1 at room temperature for 3 h gave a yellow insoluble micro-crystalline precipitate of the neutral complexes **5** and **6**, respectively. The $^{31}P\{1H\}$ NMR spectra of **5** and **6** show single peaks at 51.62 and 57.69 ppm, respectively, in line with the values previously observed for similar compounds [38,39] (see Supplementary information Fig. 1). In the $^{13}C\{1H\}$ NMR spectra of **5** and **6**, $J(^{31}P\text{–}^{13}C)$ coupling constants for the carbons of the phenyl rings were recorded, which are consistent with the literature values [40–43]. The most relevant signals of the $^{13}C\{1H\}$ NMR spectra of complexes **5** and **6** are those corresponding to the arene ligands (*p*-cymene). The carbon atoms of the arene rings in the *p*-cymene ligands are observed as two singlets at 91.35 and 85.41 ppm in compound **5** and 89.53 and 86.90 ppm in compound **6**. Furthermore, ^1H NMR spectral data of **5** and **6** are consistent with the structures proposed. In the ^1H NMR spectra, **5** and **6** are characterized by the isopropyl methyl doublets of the *p*-cymene groups, at δ 0.88 and 1.25 ppm and η^6-arene doublets at δ 5.28, 5.14 and 5.06, 4.84 ppm, respectively (for details see Section 3). In addition, the structural compositions of complexes **5** and **6** have been confirmed by IR and elemental analysis.

N,N-bis(diphenylphosphino)isopropylanilines $(PPh_2)_2N\text{–}C_6H_4\text{–}CH(CH_3)_2$, having an isopropyl substituent at carbon 2- (**3**) or 4- (**4**), were easily prepared from the reaction of $H_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2$ or $H_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2$, respectively, with two equivalents of chlorodiphenylphosphine in the presence of triethylamine in thf solution at 0 °C [44]. Attempts to prepare *N,N*-bis(diphenylphosphino)-2,6-diisopropylaniline did not succeed, possibly due to the steric repulsion between the two isopropyl groups and phenyl rings of the phosphine. We also examined some simple coordination chemistry of **3** and **4** with the $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ precursor. The complexation reactions were straightforward, with coordination to ruthenium being carried out at room temperature. Complexes **7** and **8** were formed as fine powders (Scheme 1). The reactions between the Ru(II) precursor and the bis(phosphino)amine ligands **3** and **4** were not affected by the molar ratio of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ nor by the steric and electronic properties of the donor phosphorus atoms. The reaction of $(PPh_2)_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2$, **3** and $(PPh_2)_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2$, **4** with $Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$ in CH_2Cl_2 solution in a molar ratio of 1:1/4 at room temperature for 4 h gives an orange/red solution. The solution was concentrated and cooled to 0 °C. The *trans* isomers of **7** and **8** were isolated as indicated by singlets in the $^{31}P\{1H\}$ NMR spectra at (δ) 79.65 and 79.25 ppm, respectively, in line with the values previously observed for similar compounds [45,46] (see Supplementary information Fig. 1), indicating that **3** and **4** act as bis(bidendate) chelating ligands. Furthermore, the ^1H and $^{13}C\{1H\}$ NMR spectroscopies are in agreement with the structures proposed, and the structural compositions of complexes **7** and **8** were further confirmed by IR spectroscopy and the microanalyses were found to be in good agreement with the theoretical values.

2.2. Catalytic transfer hydrogenation of acetophenone derivatives

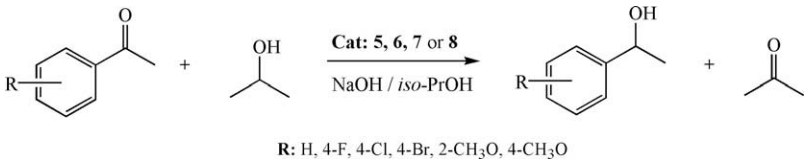
The obtained complexes **5**–**8** were then examined for the ruthenium catalyzed transfer hydrogenation of arylketones to the corresponding alcohols in *iso*-PrOH solution (Scheme 2).

In a preliminary study, if the reaction was activated by an alkoxide base, the synthesized complexes **5**–**8** were evaluated as a precursor for the catalytic transfer hydrogenation of acetophenone



5: [Ru(*p*-cymene)(*N*-diphenylphosphino)-(2-isopropylaniline)Cl_2]
6: [Ru(*p*-cymene)(*N*-diphenylphosphino)-(2,6-diisopropylaniline)Cl_2]
7: [Ru(*N,N*-bis(diphenylphosphino)-(2-isopropylaniline)Cl_2]
8: [Ru(*N,N*-bis(diphenylphosphino)-(4-isopropylaniline)Cl_2]

Scheme 1. Synthesis of the complexes $[Ru(\eta^6\text{-}p\text{-cymene})(PPh_2NH\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2)Cl_2]$ **5**, $[Ru(\eta^6\text{-}p\text{-cymene})(PPh_2NH\text{–}C_6H_3\text{-}2,6\text{-}(CH(CH_3)_2)_2)Cl_2]$ **6**, $[Ru((PPh_2)_2N\text{–}C_6H_4\text{-}2\text{-}CH(CH_3)_2)_2Cl_2]$ **7** and $[Ru((PPh_2)_2N\text{–}C_6H_4\text{-}4\text{-}CH(CH_3)_2)_2Cl_2]$ **8** (i) 1 equiv. Ph_2PCl, 1 equiv. Et_3N, thf/CH_2Cl_2 (1/2) for **1** and CH_2Cl_2 for **2**; (ii) 2 equiv. Ph_2PCl, 2 equiv. Et_3N, thf; (iii) 1/2 equiv. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$, thf; (iv) 1/4 equiv. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-}Cl)Cl]_2$, thf.



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

by *iso*-PrOH/NaOH as a reducing system. The results are summarized in Table 1. The activity of the ruthenium(II) *p*-cymene complexes is well known in this catalytic process [47–49]. The catalytic activities of complexes **5**–**8** were not deeply investigated, because of their instability in solution. At room temperature no appreciable formation of 1-phenylethanol was observed (Table 1, entries 1, 2, 3 and 4) 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 Table 1 (entries 5, 6, 7 and 8), 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 a proton of the alcohol and subsequently the 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 the ruthenium-catalyzed transfer hydrogenation reaction by metal hydride intermediates [50–52].

As Table 1 shows, high conversions can be achieved with the **5**–**8** catalytic systems. Next, we have expanded the substrate-to-catalyst ratio to observe its effect on the catalytic efficiency. As shown in Table 1, increasing the substrate-to-catalyst ratio does not damage the yields of the product in most cases. Remarkably, the transfer hydrogenation of acetophenone could be achieved in 95% yield even when the substrate concentration was increased from 0.1 to 0.5 M and the substrate-to-catalyst ratio reached 1000:1. In addition, performing the reaction in air, slowed down the reaction but did not affect yield of the product. Amazingly, the reaction was not affected by the addition of water (Table 1, entries 21 and 22). The results obtained from the optimization studies indicate clearly that excellent yields were achieved in the reduction of acetophenone to 1-phenylethanol when **5**–**8** were used as the catalytic precursor with a substrate–catalyst molar ratio (100:1) in 2-propanol, containing a small amount of NaOH at 82 °C.

Following the optimization studies, we also examined the transfer hydrogenations of aromatic ketones using complexes **5**–**8**. These results are presented in Table 2. The catalytic reduction of aromatic ketones was conducted with a substrate/catalyst molar ratio (S/C) of 100 using a 0.1 M solution in *iso*-PrOH, containing small amount of NaOH as a cocatalyst. The reduction of aromatic ketones under identical conditions using complexes **5**–**8** led to the corresponding alcohols in good to excellent yields (92–99%). As already stated, the nature and position of the substituents in the aromatic ketones result in significant effects on the activity [53,54]. Ketones with an electron-withdrawing substituent are reduced smoothly with a high rate, while the introduction of an electron-donating substituent, such as methoxy, to the *p*-position tends to lower the rate. The *p*-substituted acetophenone with the electron donor substituent 4′-methoxy is reduced more slowly than acetophenone. Notably, with an electron-donating methoxy group in the *o*-position the reaction is accelerated, but when the *p*-position is substituted the rate is lowered. Furthermore, the transfer hydrogenation of aromatic ketones with an electron-withdrawing group such as a fluoro, chloro and bromo in the *p*-position led to high conversions (up to 99%). Among all the selected ketones, the best results were obtained from the reduction of *p*-fluoroacetophenone, giving 99% conversions (Table 2, entries 2, 8, 14 and 20).

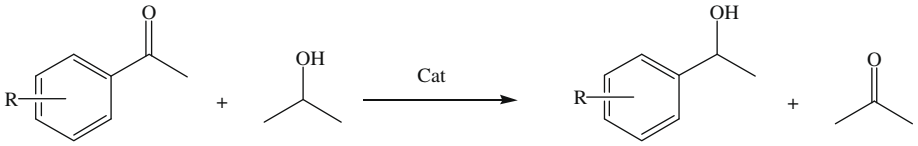
Table 1
Transfer hydrogenation of acetophenone with *iso*-PrOH catalyzed by $[Ru(\eta^6\text{-p-cymene})(PPh_2NH\text{–}C_6H_4\text{-2-}CH(CH_3)_2)Cl_2]$ **5**, $[Ru(\eta^6\text{-}p\text{-cymene})(PPh_2NH\text{–}C_6H_3\text{-2,6-}(CH(CH_3)_2)_2)Cl_2]$ **6**, $[Ru((PPh_2)_2N\text{–}C_6H_4\text{-2-}CH(CH_3)_2)_2Cl_2]$ **7** and $[Ru((PPh_2)_2\text{-}N\text{–}C_6H_4\text{-4-}CH(CH_3)_2)_2Cl_2]$ **8**.

Entry	Catalyst	S/C/NaOH	Time	Conversion (%)[h]	TOF[i]
1	5[a]	100:1:5	1 h	<1	
2	6[a]	100:1:5	1 h	<1	
3	7[a]	100:1:5	1 h	<1	
4	8[a]	100:1:5	1 h	<1	
5	5[b]	100:1	1 h (24 h)	<1 (60)	
6	6[b]	100:1	1 h	<1	
7	7[b]	100:1	1 h	<1	
8	8[b]	100:1	1 h	<1	
9	5[c]	500:1:5	2 h	98.7	49
10	6[c]	500:1:5	2 h	97.6	49
11	7[c]	500:1:5	4 h	96.8	24
12	8[c]	500:1:5	4 h	97.4	24
13	5[d]	1000:1:5	3.5 h	98.7	28
14	6[d]	1000:1:5	3.5 h	98.0	28
15	7[d]	1000:1:5	6 h	96.6	16
16	8[d]	1000:1:5	6 h	97.4	16
17	5[e]	100:1:5	15 min	49.7	199
18	6[e]	100:1:5	15 min	44.6	178
19	7[e]	100:1:5	15 min	23.6	94
20	8[e]	100:1:5	15 min	24.4	98
21	5[f]	100:1:5	4 h	99.2	25
22	5[g]	100:1:5	2 h	98.8	49

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

It is noteworthy that the Ru–aminophosphine catalytic systems, **5** and **6**, and Ru–bis(phosphino)amine catalytic systems, **7** and **8**, display differences in reactivity (Table 2). The Ru–aminophosphine complexes have proved to be excellent catalyst precursors in transfer hydrogenation of acetophenone derivatives, leading to the corresponding alcohols (in up to 94–99% yield). That is to say, the catalyst activities in the studied hydrogen transfer reactions were generally much higher for the Ru–aminophosphine complexes **5** and **6** than for the Ru–bis(phosphino)amine complexes **7** and **8**. For example, under identical conditions, transfer hydrogenation of acetophenone derivatives with the system Ru–aminophosphines led to 92–99% conversions within 30 min, whereas with Ru–bis(phosphino)amines as the auxiliary, the same 92–99% conversions were achieved only after a 1 h period (Table 2). The higher catalytic activity can be explained by the inherent hemilabile character [55] of the aminophosphine ligands which can generate an open coordination site at ruthenium more easily, thus allowing a faster substrate complexation. Complex **5** or **6**, with sp^3-hybridized nitrogen containing N–H bonds, displayed higher reaction rates. On the other hand, with the presence of N–H groups in the ligands it is possible to stabilize a six membered cyclic transition state by

Table 2
Transfer hydrogenation results for substituted acetophenones with the catalyst systems prepared from [Ru(η⁶-*p*-cymene)(μ-Cl)Cl]$_2$ and $PPh_2NH–C_6H_4$-2-$CH(CH_3)_2$ **1**, $PPh_2NH–C_6H_3$-2,6-$(CH(CH_3)_2)_2$ **2**, $(PPh_2)_2N–C_6H_4$-2-$CH(CH_3)_2$ **3** and $(PPh_2N–C_6H_4$-4-$CH(CH_3)_2$ **4**.[a]



Entry	Catalyst	R	Time	Yield (%)[b]	TOF (h^{-1})[c]
1	5	H	30 min	95.6	191
2		4-F	30 min	98.9	198
3		4-Cl	30 min	97.5	197
4		4-Br	30 min	96.3	193
5		2-MeO	30 min	96.0	192
6		4-MeO	30 min	95.0	190
7	6	H	30 min	94.3	189
8		4-F	30 min	98.4	197
9		4-Cl	30 min	97.0	194
10		4-Br	30 min	95.9	192
11		2-MeO	30 min	93.3	187
12		4-MeO	30 min	92.8	186
13	7	H	1 h	96.2	96
14		4-F	1 h	98.5	99
15		4-Cl	1 h	96.3	96
16		4-Br	1 h	95.2	95
17		2-MeO	1 h	93.4	93
18		4-MeO	1 h	90.8	91
19	8	H	1 h	97.8	98
20		4-F	1 h	99.3	99
21		4-Cl	1 h	97.7	98
22		4-Br	1 h	96.5	97
23		2-MeO	1 h	94.4	94
24		4-MeO	1 h	92.6	93

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), NaOH (0.025 mmol %), 82 °C, 30 min for **5** and **6**; 1.0 h for **7** and **8**, the concentration of the 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 arylketone.
[c] TOF = (mol product/mol Cat.) × h^{-1}.

forming a hydrogen bond with the oxygen atom of the ketones [56–58].

3. Experimental

3.1. 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. Ph_2PCl, 2-isopropylaniline, 4-isopropylaniline and 2,6-di(isopropyl)aniline were purchased from Fluka and used as received. The starting material [Ru(η⁶-*p*-cymene)(μ-Cl)Cl]$_2$ [59,60] was 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{1H} NMR spectra (162.0 MHz) were recorded on a Bruker Avance 400 spectrometer with δ referenced to external TMS and 85% H_3PO_4. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded on a Gallenkamp Model apparatus with open capillaries.

3.1.1. Synthesis of [Ru(η⁶-*p*-cymene)($PPh_2NH–C_6H_4$-2-$CH(CH_3)_2$)Cl_2], (**5**)

A mixture of [Ru(η⁶-*p*-cymene)(μ-Cl)Cl]$_2$ (0.096 g, 0.156 mmol) and $PPh_2NH–C_6H_4$-2-$CH(CH_3)_2$ (0.100 g, 0.313 mmol) in 30 mL of thf was stirred at room temperature for 3 h. The volume of the solvent was reduced to 0.5 mL before addition of diethyl ether (10 mL) to precipitate an orange micro-crystalline solid that was isolated by filtration and dried *in vacuo*. Yield 180 mg, 92%, m.p. = 175–177 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 8.15–8.02 (dd, 4H, ^5J = 6.60 and ^3J = 8.40 Hz, *o*-protons of phenyls), 7.55–7.40 (m, 6H, *m*- and *p*-protons of phenyls), 7.05 (d, 1H, ^3J = 6.80 Hz, *H-3*), 6.68 (dd, 1H, ^3J = 6.80 and 7.00 Hz, *H-4*), 6.59 (dd, 1H, ^3J = 7.00 and 8.00 Hz, *H-5*), 6.29 (d, 1H, ^3J = 8.00 Hz, *H-6*), 6.01 (d, 1H, $^2J_{NHP}$ = 12.40 Hz, N*H*-P), 5.28 (d, 2H, ^3J = 4.80 Hz, aromatic protons of *p*-cymene), 5.14 (d, 2H, ^3J = 5.20 Hz, aromatic protons of *p*-cymene), 3.36 (m, 1H, –C*H*– of aniline), 2.61 (m, 1H, –C*H*– of *p*-cymene), 1.85 (s, 3H, CH_3-Ph of *p*-cymene), 1.20 (d, 6H, ^3J = 6.40 Hz, (CH_3)$_2$CHPh of aniline), 0.88 (d, 6H, ^3J = 6.80 Hz, (CH_3)$_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 17.28 (*C*H_3Ph of *p*-cymene), 21.35 ((*C*H_3)$_2$CHPh of *p*-cymene), 23.04 ((*C*H_3)$_2$CHPh of aniline), 26.74 (–*C*H– of aniline), 30.23 (–*C*H– of *p*-cymene), 85.41, 91.35 (aromatics carbons of *p*-cymene), 93.66, 108.93 (quaternary carbons of *p*-cymene), 117.97 (*C-6*), 120.60 (*C-4*), 124.83 (*C-5*), 125.41 (*C-3*), 128.12 (d, ^3J = 10.06 Hz, *m*-carbons of phenyls), 130.79 (s, *p*-carbons of phenyls), 132.55 (d, ^2J = 11.1 Hz, *o*-carbons of phenyls), 133.28 (d, ^1J = 52.3 Hz, *i*-carbons of phenyls), 138.45 (*C-2*), 138.63 (d, ^2J = 5.5 Hz, *C-1*); assignment was based on ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 51.62 (s, –NH–*P*–(C_6H_5)$_2$–Ru); IR, (KBr, cm^{-1}) υ: 926 (P–NH), 1440 (P–Ph), 3313 (N–H); *Anal.* Calc. for $C_{31}H_{36}NPRuCl_2$: C, 59.52; H, 5.80; N, 2.24. Found: C, 59.43; H, 5.75; N, 2.20%.

3.1.2. Synthesis of [Ru(η⁶-*p*-cymene)($PPh_2NH–C_6H_3$-2,6-$(CH(CH_3)_2)_2$)Cl_2], (**6**)

A mixture of [Ru(η⁶-*p*-cymene)(μ-Cl)Cl]$_2$ (0.085 g, 0.138 mmol) and $PPh_2NH–C_6H_3$-2,6-$(CH(CH_3)_2)_2$ (0.100 g, 0.277 mmol) in 30 mL of thf was stirred at room temperature for 3 h. The volume of the

solvent was reduced to 0.5 mL before addition of diethyl ether (10 mL) to precipitate an orange micro-crystalline solid that was isolated by filtration and dried *in vacuo*. Yield 172.9 mg, 94%, m.p. = 174–176 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 7.70 (dd, 4H, ^5J = 6.40 and ^3J = 7.60 Hz, *o*-protons of phenyls), 7.41–7.26 (m, 6H, *m*- and *p*-protons of phenyls), 6.98 (t, 1H, ^3J = 7.40 Hz, *H-4*), 6.79 (d, 2H, ^3J = 7.20 Hz, *H-3* and *H-5*), 5.23 (d, 1H, $^2J_{NHP}$ = 13.20 Hz, N*H*–P), 5.06 (d, 2H, ^3J = 6.00 Hz, aromatic protons of *p*-cymene), 4.84 (d, 2H, ^3J = 6.40 Hz, aromatic protons of *p*-cymene), 3.35 (m, 2H, –C*H*– of aniline), 2.84 (m, 1H, –C*H*– of *p*-cymene), 1.89 (s, 3H, C*H*$_3$-Ph of *p*-cymene), 1.34 (d, 6H, ^3J = 6.80 Hz, (C*H*$_3$)$_2$CHPh of aniline, (a)), 1.25 (d, 6H, ^3J = 6.80 Hz, (C*H*$_3$)$_2$CHPh of aniline, (b)) 0.63 (d, 6H, ^3J = 6.80 Hz, (C*H*$_3$)$_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 17.94 (*C*H$_3$Ph of *p*-cymene), 23.47 ((CH$_3$)$_2$-CHPh of *p*-cymene), 22.29 ((C*H*$_3$)$_2$CHPh of aniline), 27.89 (–*C*H– of *p*-cymene), 30.38 (–*C*H– of aniline), 86.90, 89.53 (aromatics carbons of *p*-cymene), 94.75, 100.60 (quaternary carbons of *p*-cymene), 123.00 (*C-4*), 126.40 (*C-3* and *C-5*), 134.80 (d, ^2J = 4.5 Hz, *C-1*), 127.28 (d, ^3J = 10.0 Hz, *m*-carbons of phenyls), 130.37 (s, *p*-carbons of phenyls), 134.01 (d, ^2J = 11.0 Hz, *o*-carbons of phenyls), 136.00 (d, ^1J = 51.3 Hz, *i*-carbons of phenyls), 148.80 (*C-2* and *C-6*); assignment was based on ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 57.69 (s, –NH–*P*–(C$_6$H$_5$)$_2$–Ru); IR, (KBr, cm^{-1}) υ: 906 (P–NH), 1440 (P–Ph), 3319 (N–H); *Anal.* Calc. for $C_{34}H_{42}NPRuCl_2$: C, 61.17; H, 6.34; N, 2.10. Found: C, 61.09; H, 6.27; N, 2.06%.

3.1.3. Synthesis of [Ru((PPh$_2$)$_2$N–C$_6$H$_4$-2-CH(CH$_3$)$_2$)$_2$Cl$_2$], (**7**)

A mixture of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.030 g, 0.050 mmol) and (PPh$_2$)$_2$N–C$_6$H$_4$-2-CH(CH$_3$)$_2$ (0.100 g, 0.20 mmol) in 30 mL of thf was stirred at room temperature for 4 h. The volume of the solvent was reduced to 0.5 mL before addition of diethyl ether (10 mL) to precipitate a bright yellow micro-crystalline solid that was isolated by filtration and dried *in vacuo*. Yield 106.8 mg, 91%, m.p. > 250 °C (dec.). ^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 7.56–6.85 (m, 40H, *o*-, *m*- and *p*-protons of phenyls and 8H, aromatic protons of aniline), 3.32 (m, 2H, –C*H*– of aniline), 1.23 (d, 12H, ^3J = 6.40 Hz, (C*H*$_3$)$_2$CHPh of aniline); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 23.51 ((*C*H$_3$)$_2$CHPh of aniline), 27.34 (–*C*H– of aniline), 124.12, 126.47, 126.98, 127.10, 134.38, 139.13 (aromatic carbons of aniline), 125.69 (*m*-carbons of phenyls), 128.57 (*p*-carbons of phenyls), 129.69 (*i*-carbons of phenyls), 134.38 (*o*-carbons of phenyls); assignment was based on ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 79.65 (s, –N–(*P*–(C$_6$H$_5$)$_2$)$_2$–Ru); IR, (KBr, cm^{-1}) υ: 1438 (P–Ph), 947 (P–N); *Anal.* Calc. for $C_{66}H_{62}N_2P_4RuCl_2$: C, 67.23; H, 5.30; N, 2.38. Found: C, 67.17; H, 5.23; N, 2.33%.

3.1.4. Synthesis of [Ru((PPh$_2$)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)$_2$Cl$_2$], (**8**)

A mixture of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.030 g, 0.050 mmol) and (PPh$_2$)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$ (0.100 g, 0.20 mmol) in 30 mL of thf was stirred at room temperature for 4 h. The volume of the solvent was reduced to 0.5 mL before addition of diethyl ether (10 mL) to precipitate a bright yellow micro-crystalline solid that was isolated by filtration and dried *in vacuo*. Yield 103.8 mg, 89%, m.p. > 250 °C (dec.). ^{1}H NMR (400.1 MHz, $CDCl_3$) δ: 7.40–7.07 (m, 40H, *o*-, *m*- and *p*-protons of phenyls), 6.92 (d, 4H, ^3J = 8.40 Hz, *H-3* and *H-5*), 6.83 (d, 4H, ^3J = 8.00 Hz, *H-2* and *H-6*), 2.75 (m, 2H, –C*H*– of aniline), 1.14 (d, 12H, ^3J = 6.80 Hz, (C*H*$_3$)$_2$CHPh of aniline); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 23.75 ((*C*H$_3$)$_2$CHPh of aniline), 33.27 (–*C*H– of aniline), 126.11 (*C-2* and *C-6*), 127.10 (*C-3* and *C-5*), 126.78 (*m*-carbons of phenyls), 129.44 (s, *p*-carbons of phenyls), 133.29 (*i*-carbons of phenyls), 134.28 (*o*-carbons of phenyls), 141.29 (*C-4*), 145.30 (*C-1*); assignment was based on ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 79.25 (s, –N–(*P*–(C$_6$H$_5$)$_2$)$_2$–Ru); IR, (KBr, cm^{-1}) υ: 1436 (P–Ph), 934 (P–N); *Anal.* Calc. for $C_{66}H_{62}N_2P_4RuCl_2$: C, 67.23; H, 5.30; N, 2.38. Found: C, 67.15; H, 5.24; N, 2.32%.

3.2. Typical procedure for the transfer hydrogenation

Typical procedure for the catalytic hydrogen transfer reaction: a solution of the ruthenium complex [Ru(η^6-*p*-cymene)(PPh$_2$NH–C$_6$H$_4$-2-CH(CH$_3$)$_2$)Cl$_2$] **5** (0.005 mmol), [Ru(η^6-*p*-cymene)(PPh$_2$-NH–C$_6$H$_3$-2,6-(CH(CH$_3$)$_2$)$_2$)Cl$_2$] **6** (0.005 mmol), [Ru((PPh$_2$)$_2$N–C$_6$-H$_4$-2-CH(CH$_3$)$_2$)$_2$Cl$_2$] **7** (0.005 mmol) or [Ru((PPh$_2$)$_2$N–C$_6$H$_4$-4-CH(CH$_3$)$_2$)$_2$Cl$_2$] **8** (0.005 mmol), NaOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed iso-propanol (5 mL) were refluxed for 30 min for **5** and **6**, 60 min for **7** and **8**. After this time a sample of the reaction mixture was taken off, diluted with acetone and analyzed immediately by GC. Yields obtained are related to the residual unreacted ketone.

3.3. GC analyses

GC analyses were performed on a HP 6890 N Gas Chromatograph equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane) (30 m × 0.32 mm × 0.25 μm). The GC parameters for transfer hydrogenation of ketones were 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. Conclusion and perspectives

In conclusion, we have synthesized and characterized a series of new ruthenium(II) complexes based on aminophosphine and bis(phosphine)amine ligands which are valuable for the transfer hydrogenation of aromatic ketones. The catalysis attains a high efficiency using the ruthenium(II) complexes with aminophosphine monodendate ligands. The high catalytic activity is contrasted to the slightly lower reactivity of a structurally similar bis(phosphino)amine-based complex. The results suggest that the NH moiety in the aminophosphine ligand is responsible for the high reactivity. Further studies of other transition metal complexes of these ligands and their application in catalytic reactions are in progress. Furthermore, future investigations are aimed at the development of an asymmetric version of this process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.12.035.

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