Anilin temelli aminofosfinler ve katyonik bis(fosfino)amin Ru(II) kompleksleri: Ketonların transfer hidrojenasyonundaki katalitik aktiviteleri

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Özet

Hidrojen transfer indirgenme reaksiyonu, işlem kolaylığı avantajından dolayı sentez alanında çalışan kimyacıların ilgisini çekmektedir. Bu bağlamda, $[Ru(\eta^6\text{-}p\text{-simen})(\mu\text{-Cl})Cl]_2$ kompleksinden yola çıkarak NPP ve NHP ligandlarının bir dizi Ru(II) kompleksi sentezlendi ve bu kompleksler analitik ve spektroskopik metotlarla tam olarak karakterize edildi. **1 - 4** kompleksleri hidrojen kaynağı olarak izopropil alkol varlığında birçok alkil ve aril alkil ketonların sekonder alkollere transfer hidrojenasyonunu katalizlemektedir. Özellikle **3** nolu kompleks mükemmel bir katalizör olarak davranmakta ve ilgili alkolleri % 99 a varan dönüşümlerle sağlamaktadır (TOF:198 h^{-1}).

Anahtar Kelimeler: Aminofosfin, Bis(fosfino)amin, Transfer hidrojenasyon, Rutenyum, Kataliz, Keton.

Aniline based aminophosphine and cationic bis(phosphino)amine Ru(II) complexes: Investigation of catalytic activity in transfer hydrogenation of ketones

Abstract

Hydrogen transfer reduction processes are attracting increasing interest from synthetic chemists in view of their operational simplicity. For this aim, a series of Ru(II) complexes with the NPP and NHP ligands were synthesized starting from the complex $[Ru(\eta^6\text{-}p\text{-simen})(\mu\text{-Cl})Cl]_2$. The complexes were fully characterized by analytical and spectroscopic methods. Complexes 1-4 catalyze the transfer hydrogenation of a variety of simple alkyl and aryl alkyl ketones to secondary alcohols in the presence of *iso*-PrOH as the hydrogen source. Notably 3 acts as an excellent catalyst giving the corresponding alcohols in excellent conversions up to 99% (TOF:198 h^{-1}).

Keywords: Aminophosphine, Bis(phosphino)amine, Transfer hydrogenation, Ruthenium, Catalysis, Ketone.

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1. Introduction

Today, the catalytic transfer hydrogenation [1] of prochiral ketones is one of the most attractive methods for synthesizing optically active secondary alcohols, which form an important class of intermediates for fine chemicals and pharmaceuticals [2,3]. Transition metal catalyzed procedures for transfer hydrogenation of a wide variety of functional groups by different hydrogen donors are an interesting alternative to conventional catalytic hydrogenation. 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]. The only side product is acetone, which is easily removed by distillation during workup and it is a solvent that does not affect pH and therefore it is preferred over formic acid as hydrogen donor [5].

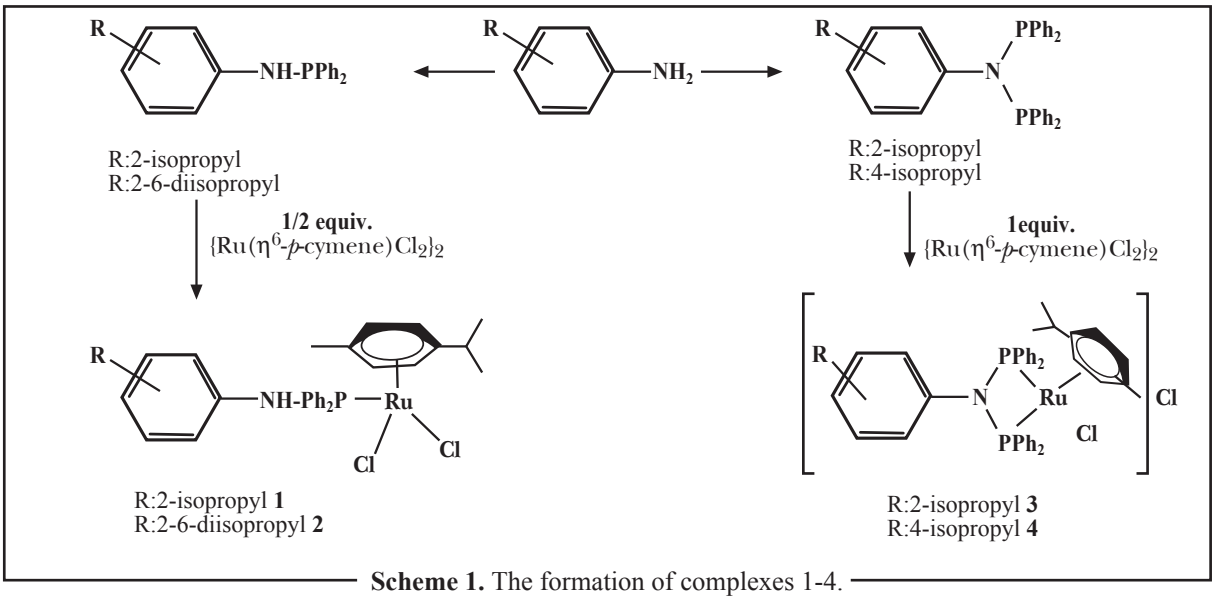
Ruthenium complexes containing suitable combinations of P and N or mixed PN ligands have proven to be highly efficient catalysts for the hydrogenation and transfer hydrogenation of carbonyl compounds. Thus, bi-, tri-, and tetradentate achiral and chiral ligands have successfully been used to prepare five- and six-coordinate complexes for the transfer hydrogenation [6]. Synthesis and coordination chemistry of bis(phosphino)anilines have also been studied in some detail [7,8]. It has been shown that coordination of bis (phosphino) anilines to transition metal ions occurs mainly via the phosphorus centers due to the low basicity of the amine nitrogen, attributable to the P–N_π interaction between the phosphorus d_π and nitrogen p_π orbitals [9,10].

Recently, we reported the synthesis and application of aniline based ruthenium complexes in transfer hydrogenation reactions [11,12]. Herein, we report that these complexes also form efficient catalysts for the transfer hydrogenation of various simple alkyl and aryl alkyl ketones with *iso*-PrOH under varying conditions.

2. Result and Discussion

2.1. Synthesis of the complexes

We have previously described [11,12] the synthesis of [Ru(η^6-*p*-cymene)(PPh_2NH–C_6H_4-2-$CH(CH_3)_2$)Cl_2] **(1)**, [Ru(η^6-*p*-cymene)(PPh_2NH–C_6H_3–2,6-$(CH(CH_3)_2)_2$)Cl_2] **(2)**, [Ru($(Ph_2P)_2N$-C_6H_4-2-$CH(CH_3)_2$)(η^6-*p*-cymene)Cl]Cl, **(3)** and [Ru($(Ph_2P)_2N$-C_6H_4-4-$CH(CH_3)_2$)(η^6-*p*-cymene)Cl]Cl **(4)**, respectively, as shown in Scheme 1. The reactions of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ with PPh_2NH–C_6H_4-2-$CH(CH_3)_2$ and PPh_2NH–C_6H_3-2,6-$(CH(CH_3)_2)_2$ in CH_2Cl_2 in a ratio of 1/2:1 at room temperature for 3 h gave orange insoluble micro-crystalline precipitate of the neutral complexes **1** and **2**, respectively. The $^{31}P\{^1H\}$ NMR spectra are quite consistent with the structures [13], that of containing **1** or **2**. In the ^1H NMR spectra, **1** and **2** are characterized by the isopropyl methyl doublets of the *p*-cymene groups, at δ 0.88 and 1.25 ppm, methyl singlets of the *p*-cymene at δ 1.85 and 1.89 ppm, and -CH- of the *p*-cymene δ 2.61(m, 1H) and 2.84 ppm (m, 1H), respectively. In the $^{13}C\{^1H\}$ NMR spectra of compounds **1** and **2**, alkyl carbon atoms in *p*-cymene ligands are observed as three signals at 17.28, 21.35 and 30.23 ppm in complex **1** and 17.94, 23.47 and 27.89 ppm in complex **2.** Treatment of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ with one equivalent of $(PPh_2)_2N$-C_6H_4-2-$CH(CH_3)_2$, or $(PPh_2)_2N$-C_6H_4-4-$CH(CH_3)_2$, affords the corresponding mono bis(chelate) complexes in high yield as the main products, respectively (Scheme 1). The initial color change, i.e., from clear orange to deep red [14], attributed to the dimer cleavage most probably by the bis(phosphino)amine ligand. The $^{31}P\{^1H\}$ NMR spectra of **3** and **4** show single peaks at 90.71 and 86.51 ppm, respectively. Furthermore, ^1H NMR and ^{31}C NMR spectral data of **3** and **4** are consistent with the structure proposed (for details see Experimental section). The structural compositions of the complexes have also been confirmed by IR and elemental analysis.

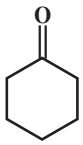
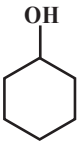
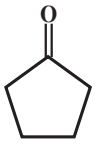
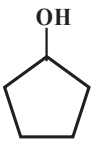
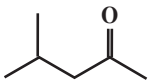
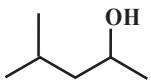
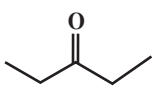
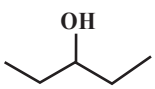


Scheme 1. The formation of complexes 1-4.

2.2. Catalytic transfer hydrogenation of ketones

The activity of Ru(II)-arene complexes is well known in the catalytic transfer hydrogenation of carbonyl compounds [15,16,17]. Recently, we have reported that the complexes, [Ru(η^6-*p*-cymene)(PPh_2NH–C_6H_4-2-$CH(CH_3)_2$)Cl_2] **(1)**, [Ru(η^6-*p*-cymene)(PPh2NH C6H3-2,6-$(CH(CH_3)_2)_2$)Cl_2] **(2)**, [Ru($(Ph_2P)_2$N-C_6H_4-2-$CH(CH_3)_2$)(η^6-*p*-cymene)Cl]Cl, **(3)** and [Ru($(Ph_2P)_2$N-C_6H_4-4-$CH(CH_3)_2$)(η^6-*p*-cymene)Cl]Cl **(4)**, are active catalysts in the reduction of acetophenone derivatives.11,12 The observed excellent activity of these comp-

Table 1. Transfer hydrogenation of various simple ketones with iso-PrOH catalyzed by complexes 1-4.

Entry	Catalyst	Time	Substrate	Product	Conversion (0/0)[b]	TOF(h^{-1})[c]
1	1	60 min			98	98
2	2	60 min			97	97
3	3	30 min			98	196
4	4	60 min			96	96
5	1	60 min			99	99
6	2	60 min			98	98
7	3	30 min			98	196
8	4	60 min			97	97
9	1	3 h			97	32
10	2	3 h			97	32
11	3	1.5 h			98	65
12	4	3 h			97	32
13	1	6 h			98	16
14	2	6 h			96	16
15	3	3 h			97	32
16	4	6 h			97	16

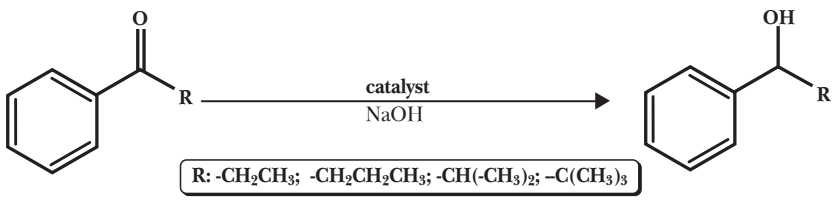
[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), NaOH (0.025 mmol %), 82 ^{0}C, the concentration of simple ketones is 0.1 M,

[b] Purity of compounds is checked by ^{1}H NMR and GC (three independent catalytic experiments), yields are based on alkyl ketone,

[c] TOF = (mol product/mol Cat.) x h^{-1}.

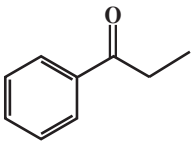
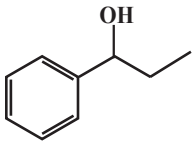
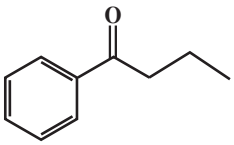
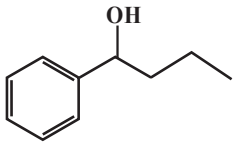
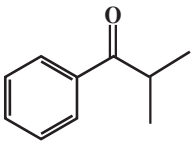
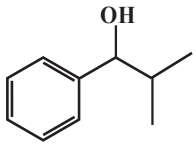
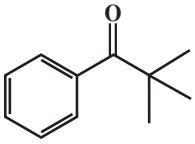
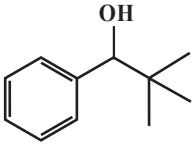
lexes has prompted us to investigate their activity for other simple ketones. For this reason, we tested catalytic activity tests using the complexes **1-4** in the transfer hydrogenation of a various simple ketones to the corresponding alcohols in *iso*-PrOH solution. Investigation of catalytic activity these complexes has shown that they are efficient catalysts affording almost quantitative transformation of the ketones. It is noteworthy that these complexes display the differences in reactivity and complex **3** is more active than complexes **1, 2** and **4** (Table 1). For instance, under identical conditions, hydrogenation of cyclohexanone with complex **3** led to 98 % within 30 min, whereas with complex **4** as the auxiliary, the same to 96 % conversions were achieved only after a 1h period (Table 1 entry 3, 4). Thus, it can be concluded that **3** is more active than **4** which are similar structures except position of isopropyl substituent on aniline ring. This indicates importance of position of the substituent on catalytic activity.

We also carried out further experiments to investigate the effect of bulkiness of the alkyl groups on the catalytic activity (Scheme 2) and the results were given in Table 2 (Entries 1–16). A variety of simple aryl alkyl ketones were transformed to the corresponding secondary alcohols. Conversion of propiophenone occurred in 20 min by **3** and 40 min by **1, 2** and **4** (entry 1-4), while that of 2-methylpropiophenone occurred in 1 h by **3** and 2 h by **1, 2** and **4** (entry 9-12). Therefore, it was found that the activity is highly dependent on the steric hindrance of the alkyl group and the reactivity gradually decreased by increasing the bulkiness of the alkyl groups [18,19,20].



Scheme 2. General reaction scheme for the metal-catalyzed hydrogen transfer from *iso*-PrOH to various aryl alkyl ketones.

Table 2. Transfer hydrogenation of substituted alkyl phenyl ketones with iso-PrOH catalyzed by complexes 1-4.

Entry	Catalyst	Time	Substrate	Product	Conversion (0/0)[b]	TOF(h^{-1})[c]
1	1	40 min			98	147
2	2	40 min			97	146
3	3	20 min			98	294
4	4	40 min			96	146
5	1	60 min			99	99
6	2	60 min			98	98
7	3	30 min			99	198
8	4	60 min			97	97
9	1	2 h			97	49
10	2	2 h			97	49
11	3	60 min			98	98
12	4	2 h			98	49
13	1	3 h			98	33
14	2	3 h			98	33
15	3	1.5 h			97	65
16	4	3 h			98	33

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), NaOH (0.025 mmol %), 82 °C, the concentration of alkyl phenyl ketones is 0.1 M,

[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on alkyl aryl ketone,

[c] TOF = (mol product/mol Cat.) x h^{-1}.

3. Conclusions

In conclusion, we have synthesized [Ru(η^6-*p*-cymene)(PPh_2NH-C_6H_4-2-$CH(CH_3)_2$)Cl_2] **(1)**, [Ru(η^6-*p*-cymene)(PPh_2NH-C_6H_3-2,6-$(CH(CH_3)_2)_2$)Cl_2] **(2)**, [Ru($(Ph_2P)_2N$-C_6H_4-2-$CH(CH_3)_2$)(η^6-*p*-cymene)Cl]Cl, **(3)** and [Ru($(Ph_2P)_2N$-C_6H_4-4-$CH(CH_3)_2$)(η^6-*p*-cymene)Cl]Cl, **(4)** and found that these complexes are efficient homogeneous catalytic systems that can be readily implemented and lead to secondary alcohols from good to excellent yields. Furthermore, the influence of position of substituent on aniline ring in the catalytic transfer hydrogenation of ketones was also investigated and found that it affected catalytic activity for cationic Ru-bis (phosphino)amine complexes, whereas it did not have any influence on catalytic activity for Ru-aminophosphine complexes.

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-isopropylaniline, 2,6-isopropylaniline and 4-isopropylaniline are purchased from Fluka and were used as received. [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ [21,22] 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-{^{1}H} NMR spectra (162.0 MHz) were recorded on a Bruker Avance 400 spectrometer, with d 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 a Shimadzu 2010 Plus Gas Chromatograph equipped with capillary column (5% biphenyl, 95% dimethylsiloxane) (30 mx0.32 mmx0.25 μm). The GC parameters for transfer hydrogenation of ketones were as follows; initial temperature, 110 ^{0}C; initial time, 1 min; solvent delay, 4.48 min; temperature ramp 80 ^{0}C/min; final temperature, 200 ^{0}C; final time, 21.13 min; injector port temperature, 200 ^{0}C; detector temperature, 200 ^{0}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(η^6-*p*-cymene)(PPh_2NH-C_6H_4-2-$CH(CH_3)_2$)Cl_2] **(1)**, [Ru(η^6-*p*-cymene)(PPh_2NH-C_6H_3-2,6-$(CH(CH_3)_2)_2$)Cl_2] **(2)**, [Ru($(Ph_2P)_2N$-C_6H_4-2-$CH(CH_3)_2$)(η^6-*p*-cymene)Cl]Cl, **(3)** or [Ru($(Ph_2P)_2N$-C_6H_4-4-$CH(CH_3)_2$)(η^6-*p*-cymene)Cl]Cl **(4)** (0.005 mmol), NaOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed *iso*-PrOH (5 mL) were refluxed until the reaction is completed. 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. Procedure for the preparation of ruthenium(II) complexes [11,12]

4.4.1. Synthesis of [Ru(η^6-p-cymene)(PPh_2NH C_6H_4-2-$CH(CH_3)_2$)Cl_2], (1)

A mixture of [Ru(η^6-*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 ^{0}C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ= 8.15 8.02 (dd, 4H, ^5J = 6.6 and ^3J = 8.4 Hz, *o*-protons of phenyls), 7.55–7.40 (m, 6H, *m*- and *p*- protons of phenyls), 7.05 (d, ^{1}H, ^3J = 6.8 Hz, **H**-3), 6.68

(dd, ^{1}H, ^3J= 6.8 and 7.1 Hz, **H**-4), 6.59 (dd, ^{1}H, ^3J=7.1 and 8.1 Hz, **H**-5), 6.29 (d, ^{1}H, ^3J= 8.1 Hz, **H**-6), 6.01 (d, ^{1}H, $^2J_{NHP}$ = 12.4 Hz, NH-P), 5.28 (d, 2H, ^3J= 4.8 Hz, aromatic protons of *p*-cymene), 5.14 (d, 2H, ^3J= 5.2 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= 6.4 Hz, (C**H**$_3$)$_2$CHPh of aniline), 0.88 (d, 6H, ^3J= 6.8 Hz, (C**H**$_3$)$_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ=17.28 (CH_3Ph of *p*-cymene), 21.35 ((CH$_3$)$_2$CHPh of *p*-cymene), 23.04 ((CH$_3$)$_2$CHPh of aniline), 26.74 (-CH of aniline), 30.23 (-CH 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=10.1 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%.

4.4.2. Synthesis of [Ru(η^6-*p*-cymene)(PPh$_2$NH -C$_6$H$_3$-2,6-(CH(CH$_3$)$_2$)$_2$)Cl$_2$], (2)

A mixture of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.085 g, 0.138 mmol) and PPh_2NH-C_6H_3-2,6-(CH(CH$_3$)$_2$)$_3$ (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 ^{0}C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ= 7.70 (dd, 4H, ^5J= 6.4 and ^3J= 7.6 Hz, *o*-protons of phenyls), 7.41-7.26 (m, 6H, m- and *p*-protons of phenyls), 6.98 (t, 1H, ^3J= 7.4 Hz, H-4), 6.79 (d, 2H, ^3J= 7.2 Hz, **H**-3 and **H**-5), 5.23 (d, 1H, $^2J_{NHP}$=13.2 Hz, N**H**-P), 5.06 (d, 2H, ^3J= 6.1 Hz, aromatic protons of *p*-cymene), 4.84 (d, 2H, ^3J= 6.4 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= 6.8 Hz, (C**H**$_3$)$_2$CHPh of aniline, (a)), 1.25 (d, 6H, ^3J =6.8 Hz, (C**H**$_3$)$_2$CHPh of aniline, (b)) 0.63 (d, 6H, ^3J = 6.8 Hz, (C**H**$_3$)$_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ= 17.94 (CH_3Ph of p-cymene), 23.47 ((CH$_3$)$_2$-CHPh of p-cymene), 22.29 ((CH$_3$)$_2$CHPh of aniline), 27.89 (-CH- of *p*-cymene), 30.38 (-CH- 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= 10.1 Hz, m-carbons of phenyls), 130.37 (s, *p*-carbons of phenyls), 134.01 (d, ^2J= 11.1 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_6H_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%.

4.4.3. Synthesis of [Ru((Ph$_2$P)$_2$N-C$_6$H$_4$-2-CH(CH$_3$)$_2$)(η^6-*p*-cymene)Cl]Cl, (3)

To a solution of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.122 g, 0.199 mmol) in 10 mL thf, a solution (thf, 15 mL) of (PPh$_2$)$_2$N-C$_6$H$_4$-2-CH(CH$_3$)$_2$, (0.100 g, 0.199 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 (3x15 mL) and then dried under vacuum (Scheme 1). Following recrystallization from diethylether/CH_2Cl_2, a red crystalline powder was obtained (yield 144.1 mg, 89 %), m.p. 284-285 ^{0}C. ^{1}H NMR (400.1 MHz, $CDCl_3$) δ = 6.89-7.56 (m, 20H, *o*, *m*-, p-protons of phenyls and 4H, aromatic protons of aniline), 5.45 (d, 2H, ^3J= 5.2 Hz, aromatic

protons of *p*-cymene), 5.26 (d, 2H, ^3J= 5.20 Hz, aromatic protons 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 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$(CH_3)_2$- of aniline), 22.26 ($(CH_3)_2$CHPh of *p*-cymene), 18.94 (**C**H_3Ph 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.

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

To a solution of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ (0.122 g, 0.199 mmol)in 10 mL thf, a solution (thf, 15 mL) of (PPh$_2$)$_2$N-C$_6$H$_4$-4-CH(CH$_3$)$_2$, (0.100 g, 0.199 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 (3x15 mL) and then dried under vacuum (Scheme 1). Following recrystallization from diethylether/CH_2Cl_2, a red crystalline powder was obtained (yield 150.2 mg, 93 %), m.p. 250 ^{0}C (dec.). ^{1}H NMR (400.1 MHz, $CDCl_3$) δ = 7.29-7.69 (m, 20H, *o*, *m*- and *p*-protons of phenyls), 6.80 (d, 2H, J= 7.6 Hz, **H**-3 and **H**-5), 6.63 (d, 2H, J = 8.1 Hz, **H**-2 and **H**-6), 5.52 (d, 2H, ^3J= 5.2 Hz, aromatic protons of *p*-cymene), 5.38 (d, 2H, ^3J=5.2 Hz, aromatic protons of *p*-cymene), 2.82 (m, 1H, -CH- 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= 6.6 Hz, (C**H**$_3)_2$CHPh of *p*-cymene), 1.14 (d, 6H, J=6.8 Hz, -CH(C**H**$_3)_2$ of aniline) ppm; ^{13}C 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$(CH_3)_2$ of aniline), 22.30 ($(CH_3)_2$CHPh of *p*-cymene), 18.96 (CH_3Ph 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.

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