İki çekirdekli rutenyum(II) aren komplekslerinin ketonların transfer hidrojenasyonuna uygulanması

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Özet

Geçiş metal katalizörlerinin transfer hidrojenasyon reaksiyonuyla organik substratlara hidrojen katılması veya çıkarılması önemli bir sentetik araçtır. Bu amaçla, N3,N3'-di-2-hidroksibenziliden-[2,2']bipiridinil-3,3'-diamin bileşiğinden elde edilen bir P-O ligandı olan N3,N3'-di-2-(difenilfosfino)benziliden-[2,2']bipiridinil-3,3'-diaminin bir dizi metal kompleksi sentezlendi. N3,N3'-di-2-(difenilfosfino)benziliden-[2,2']bipiridinil-3,3'-diaminin $[Ru(\eta^6\text{-benzen})(\mu\text{-Cl})Cl]_2$ yada $[Ru(\eta^6\text{-p-simen})(\mu\text{-Cl})Cl]_2$ ile reaksiyonu köprülü ve iki çekirdekli $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-benzen})Cl_2\}_2]$ **1** ve $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-p-cymene})Cl_2\}_2]$ **2**, komplekslerini vermektedir. Ru(II)-bisfosfinit kompleksleri ayrıca basit birçok alkil ve aril alkil ketonun transfer hidrojenasyonunda katalizör olarak kullanıldı ve iyi düzeyde (% 99'a kadar) dönüşümler elde edildi.

Anahtar Kelimeler: Bis(fosfinit), Transfer hidrojenasyon, Rutenyum, Kataliz, Keton.

Application of dinuclear ruthenium(II) arene complexes in transfer hydrogenation of ketones

Abstract

The ability of transition metal catalysts to add or remove hydrogen from organic substrates by transfer hydrogenation process is a valuable synthetic tool. For this aim, a series of metal complexes with a P-O ligand, N3,N3'-di-2-(diphenylphosphino)benzylidene-[2,2']bipyridinyl-3,3'-diamine derived from N3,N3'-di-2-hydroxybenzylidene-[2,2']bipyridinyl-3,3'-diamine were synthesized. Reaction of N3,N3'-di-2-(diphenylphosphino)benzylidene-[2,2']bipyridinyl-3,3'-diamine with $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ or $[Ru(\eta^6\text{-p-cymene})(\mu\text{-Cl})Cl]_2$ gave bridged dinuclear complexes $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-benzene})Cl_2\}_2]$ **1** and $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-p-cymene})Cl_2\}_2]$ **2**, respectively. Ru(II)-bisphosphinite complexes have also been used as catalysts for the transfer hydrogenation of a variety of simple alkyl and aryl alkyl ketones and good conversions (up to 99 %) were obtained.

Keywords: Bis(phosphinite), Transfer hydrogenation, Ruthenium, Catalysis, Ketone.

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1.Introduction

Environmental concerns in chemistry have increased the demand for more selective chemical processes with a minimum amount of waste ("green chemistry"). Hydrogen transfer reactions are mild methodologies for reduction of ketones or imines and oxidation of alcohols or amines in which a substrate-selective catalyst transfers hydrogen between the substrate and a hydrogen donor or acceptor, respectively [1,2,3]. Furthermore, the donor (e.g. 2-propanol) and the acceptor (e.g.a ketone or a quinone) are environmentally friendly and also easy to handle [4]. In addition, when propan-2-ol is used as hydrogen donor, 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 acis as hydrogen donor [5].

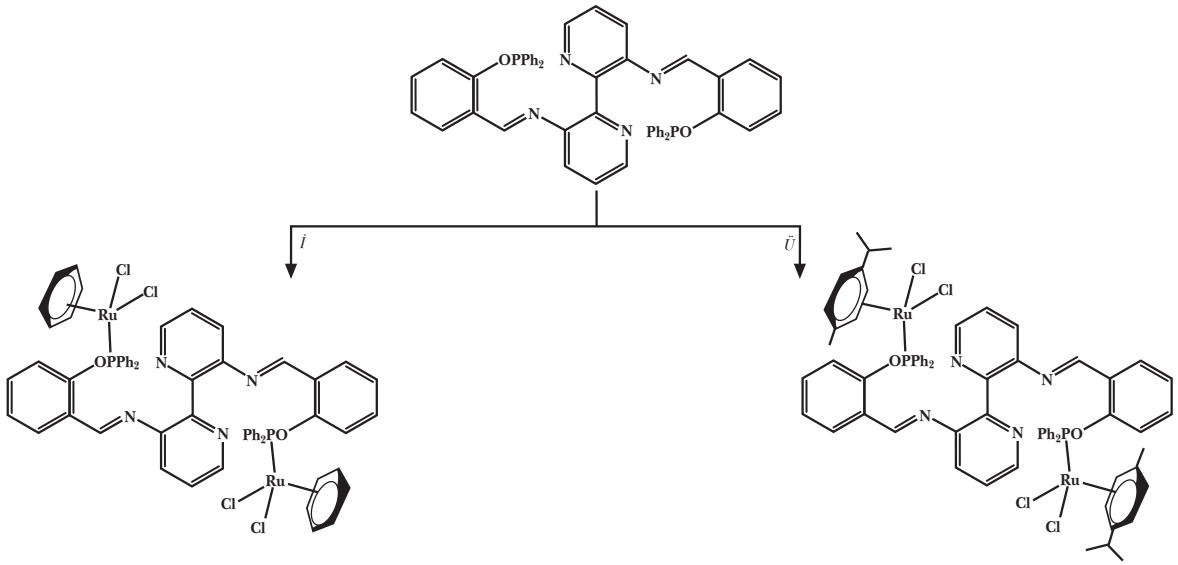
Homogeneous ruthenium complexes are considered to be the most attractive catalysts for transfer hydrogenation reactions, though other metal complexes have also been used successfully [6,7]. Varying levels of efficiency were observed for ruthenium complexes with ligands such as diamines [8], aminoalcohols [9], phosphanes [10], peptide analogues [11], ferronecyl-derivatives [12], aminophosphines [13], bis(phosphino)amine [14], phosphinite [15] and oxazoline-2-yl pyridines [16]. Also, Ru enjoys a cost advantage relative to other asymmetric hydrogenation metals such as Rh [17].

In recent years, Ru(II)-arene complexes containing monodentate or bidentate ligands have proved to be very useful in catalytic synthesis. Ru(II)-arene complexes display three-legged piano-stool structures in which the metal center has a pseudo-tetrahedral geometry[18] We paid particular attention to Ru-(η^6-arene) complexes as catalysts because (1) the aromatic spectators automatically occupy three adjacent coordination sites in an octahedral Ru coordination environment, leaving three sites with a fac relationship for other functions; (2) arene ligands may provide a unique reactivity and selectivity to the metallic center; and (3) the substitution pattern on the arene ring is flexible [19]. As part of our continuing research program on the complexes we report here the synthesis of ruthenium (II) complexes of [$(Ph_2PO)_2$-$C_{24}H_{16}N_4$]. Moreover, Ru(II) complexes of this bis (phosphinite) ligand were tested as catalyst in the transfer hydrogenation of a variety of simple alkyl and aryl alkyl ketones.

2. Result and Discussion

2.1. Synthesis of the complexes

As reported previously [20] reaction of [$(Ph_2PO)_2$-$C_{24}H_{16}N_4$] with [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ and [Ru(η^6-p-cymene)(μ-Cl)Cl]$_2$, yields complexes [$C_{24}H_{16}N_4${$OPPh_2$-Ru(η^6-benzene) Cl_2}$_2$] **1** and [$CC_{24}H_{16}N_4${$OPPh_2$-Ru(η^6-p-cymene)Cl_2}$_2$] **2**, respectively, as shown in Scheme 1. The reaction of stoichiometric amounts of [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ and [$(Ph_2PO)_2$-$C_{24}H_{16}N_4$], affords the complex [$C_{24}H_{16}N_4${$OPPh_2$-Ru(η^6-benzene)Cl_2}$_2$], **1** in good yield as a dark red microcrystalline powder. The ^{31}P-{^{1}H} NMR spectrum of **1** showed a single resonance at δ(P) 116.99 ppm, similar to those found for closely related compounds, indicative of both phosphorus being equivalent as a result of the symmetry (C_2 symmetry) of the molecule [21,22]. Analysis of complex **1** by ^{1}H NMR exhibits signals corresponding to the C_6H_6 protons as a singlet at 5.97 ppm and by ^{13}C NMR displays the C_6H_6 carbon resonance occurring at 88.12 (s) ppm. The reaction of [Ru(η^6-p-cymene)(μ-Cl)Cl]$_2$ with one equivalent of [$(Ph_2PO)_2$-$C_{24}H_{16}N_4$] in toluene at room temperature gave the red compound 2 in high conversions. [$C_{24}H_{16}N_4${$OPPh_2$-Ru(η^6-*p*-cymene)Cl_2}$_2$] **2**, was isolated as indicated by a singlet in the ^{31}P-{^{1}H} NMR spectrum at 118.05 ppm in line with the values previously observed for similar compounds [23]. Furthermore, ^{1}H NMR spectral data of **2** are consistent with the structures proposed. In the ^{1}H NMR spectrum, **2** is characterized by the η^6-arene doublets at δ 5.38 and 5.31 ppm and, the carbon atoms of the arene rings in the p-cymene ligands are

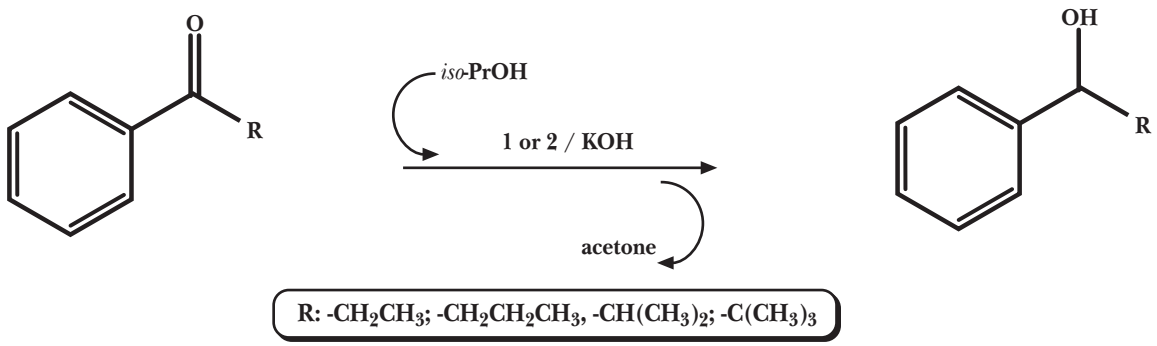


Scheme 1. The formation of complexes $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **1** and $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-p-cymene})Cl_2\}_2]$, **2**, from the reaction of $[(Ph_2PO)_2\text{-}C_{24}H_{16}N_4]$ (*i*) 1 equiv. $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, (*ii*) 1 equiv. $[Ru(\eta^6\text{-p-cymene}(\mu\text{-Cl})Cl]\eta^6$, all in toluene.

observed as two resonances at 92.58 and 87.14 ppm in the ^{13}C NMR spectrum of **2**. The structures of the **1** and **2** were further confirmed by IR spectroscopy and microanalysis and found to be in good agreement with the theoretical values (for details see experimental Section).

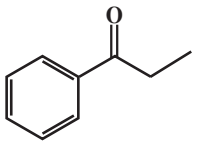
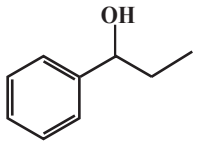
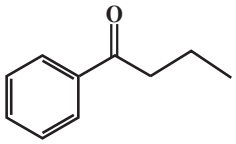
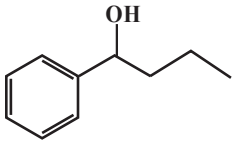
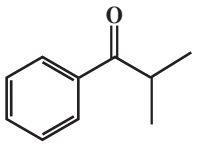
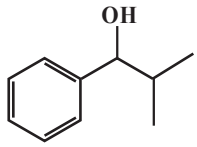
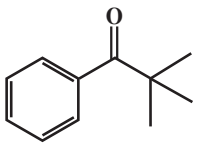
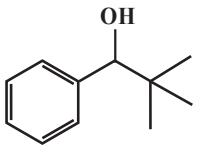
2.2. Catalytic transfer hydrogenation of ketones

The activity of Ru(II)-arene complexes is well known in the catalytic transfer hydrogenation of carbonyl compounds [24,25,26] since O P linkage possibly can stabilize a catalytic transition state [27] which, in turn, causes higher catalytic activity. Recently, we have reported that the complexes, $C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **1** and $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-p-cymene})Cl_2\}_2]$, **2**, are active catalysts in the reduction of acetophenone derivatives [15,20]. The observed excellent activity of these complexes has prompted us to investigate their activity for other aryl and alkyl ketones. For this reason, we tested catalytic activity tests using the complexes **1-2** in the transfer hydrogenation of a various aryl alkyl ketones to the corresponding alcohols in *iso*-PrOH solution (Scheme 2). In a typical experiment, 0.01 mmol of the complex and 1.0 mmol of ketone were added to a solution of KOH in *iso*-PrOH (0.05 mmol of KOH in 10 mL *iso*-PrOH) and refluxed at 82 ^{0}C. The reaction was followed by using GC. For aryl alkyl ketones, heating is generally required to achieve high conversion.



Scheme 2. Hydrogen transfer from iso-PrOH to various aryl alkyl ketones.

Table 1. Transfer hydrogenation of substituted alkyl phenyl ketones with iso-PrOH catalyzed by $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-benzene})Cl_2\}_2]$ **1** and $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-p-cymene})Cl_2\}_2]$ **2.**

Entry	Catalyst	Time	Substrate	Product	Conversion (%)[b]	TOF(h^{-1})[c]
1	1	20 min			98	294
2	2	20 min			98	294
3	1	30 min			98	196
4	2	30 min			99	198
5	1	60 min			97	97
6	2	60 min			98	98
7	1	1.5 h			98	65
8	2	1.5 h			97	65

[a] Catalyst (0.01 mmol), substrate (1 mmol), *iso*-PrOH (10 mL), KOH (0.05 mmol %), 82 ^{0}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}.

With a complex/KOH ratio of 1/5, the complexes are highly active leading to a quantitative transformation of the ketone, with a moderate TOF. The results of catalytic tests are listed in Table 1. Conversion of propiophenone occurred in 20 min by 1 or 2 (entry 1-2), respectively, while that of 2,2-dimethylpropiophenone occurred in 1.5 h by 1 or 2 (entry 7-8), respectively. It was found that the activity is highly dependent on the steric bulkiness of the alkyl group. The reactivity gradually decreased by increasing the bulkiness of the alkyl groups [28,29]. In addition, results obtained from the studies indicate clearly that both complexes are active and efficient catalysts leading to nearly quantitative conversions, with no significant difference between the catalytic activities, implying that the catalytic efficiency was not dependent on the arene ligand.

Encouraged by the high catalytic activities obtained in these preliminary studies, we next extended our investigations to include transfer hydrogenation of various simple ketones. Ruthenium-based catalysts have usually been applied in the hydrogenation of simple ketones, [30,31,32] so, we investigated catalytic activity of complexes **1-2** and the results are shown in Table 2. The catalytic performance shown by both of these complexes is higher than that of recently reported for the related half-sandwich complexes [33]. Furthermore, in order to investigate the evolution of the catalyst, **1-2**, $^{31}P\text{-}\{^1H\}$-NMR spectra were recorded periodically after the catalytic reaction. The singlet observed at 21.50 ppm at the end of third day in the spectrum is corresponding to hydrolysis product diphenylphosphinous acid, $Ph_2P(O)H$ (Figure 1) [34,35,36].

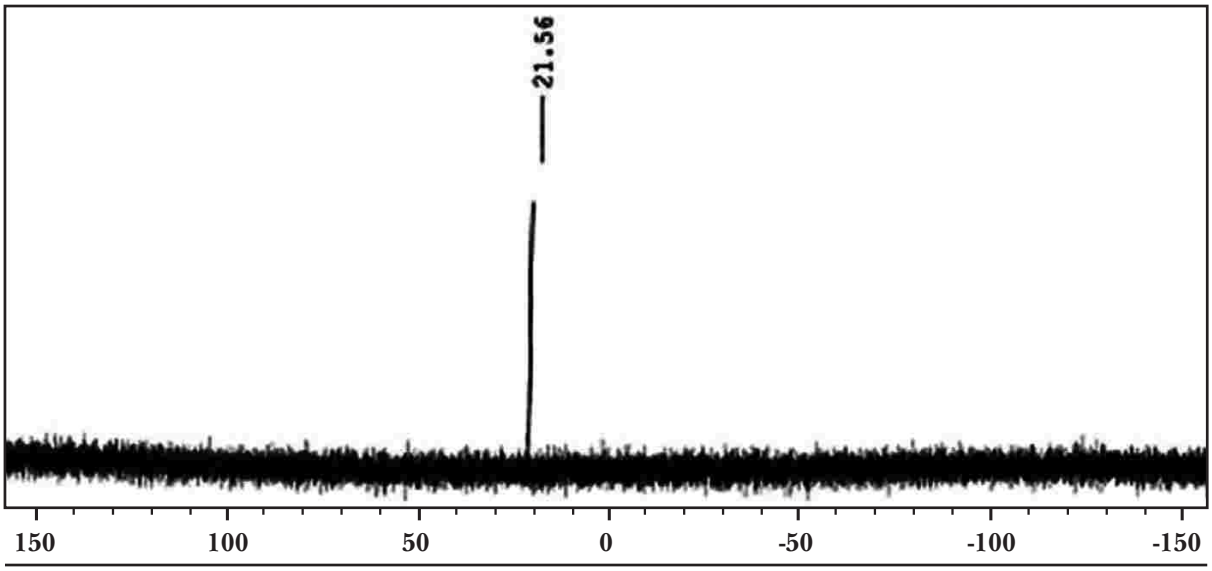
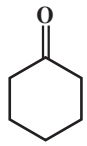
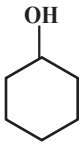
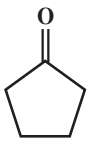
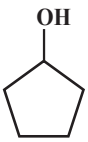
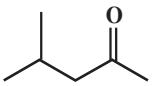
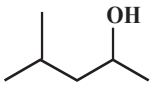
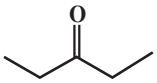
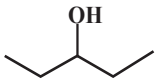


Figure 1. ^{31}P-{^{1}H}-NMR spectrum of diphenylphosphinous acid, $Ph_2P(O)H$.

Table 2. Transfer hydrogenation of various simple ketones with *iso*-PrOH catalyzed by $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-benzene})Cl_2\}_2]$ 1 and $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-p-cymene})Cl_2\}_2]$ **2.**

Entry	Catalyst	Time	Substrate	Product	Conversion (%)[b]	TOF(h^{-1})[c]
1	1	30 min			97	294
2	2	30 min			98	294
3	1	30 min			97	194
4	2	30 min			96	192
5	1	1.5 h			99	66
6	2	1.5 h			98	65
7	1	3 h			97	32
8	2	3 h			97	32

[a] Catalyst (0.01 mmol), substrate (1 mmol), *iso*-PrOH (10 mL), KOH (0.05 mmol %), 82 ^{0}C, the concentration of simple ketones is 0.1 M,

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

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

3. Conclusions

In conclusion, we have synthesized two bridged-dinuclear Ru(II) transition-metal complexes based N3,N3'-di-2-(diphenylphosphino)benzylidene-[2,2']bipyridinyl-3,3'-diamine bidendate ligand. 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. Furthermore, the influence of arene ring in the catalytic transfer hydrogenation of ketones was also investigated and found that their catalytic activities were very similiar. Furthermore, the modular construction of these catalysts and their flexibility toward transfer hydrogenation make these systems to pursue.

4. Experimental

4.1. General remarks

All reactions and manipulations were performed under argon unless otherwise stated. Ph_2PCl was purchased from Fluka and used directly. Analytical grade and deuterated solvents were purchased from Merck. Solvents were dried using the appropriate reagents and distilled prior to use. The starting materials $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, [37] $[Ru(\eta^6\text{-p-cymene})(\mu\text{-Cl})Cl]_2$, [38,39] were prepared according to literature procedures. Infrared spectra were recorded as KBr pellet in the range 4000-400 cm^{-1} on a Mattson 1000 ATI UNICAM FT-IR spectrometer. ^1H (400.1 MHz), ^{13}C NMR (100.6 MHz) and $^{31}P\text{-}\{^1H\}$ NMR (162.0 MHz) spectra were recorded on a Bruker AV400 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 on a 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 m x 0.32 mm x 0.25 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. Transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen transfer reaction: a suspension of metal complexes Ru(II) (0.01 mmol), KOH (0.05 mmol) and ketone (1 mmol) in degassed *iso*-PrOH (10 mL) was refluxed until the reaction is completed. Then a sample of the reaction mixture is taken, diluted with acetone and analyzed immediately by GC. Yields obtained are related to the residual unreacted ketone.

4.4. Procedure for the preparation of ruthenium(II) complexes [20]

4.4.1. Synthesis of $[C_{24}H_{16}N_4\{OPPh_2\text{-}Ru(\eta^6\text{-benzene})Cl_2\}_2]$, 1

To a solution of $[(\eta^6\text{-benzene})RuCl_2]_2$ (63.5 mg, 0.127 mmol) in toluene, a solution (toluene, 25 mL) of $[(Ph_2PO)_2\text{-}C_{24}H_{16}N_4]$, (96.8 mg, 0.127 mmol) was added. The resulting reaction mixture was allowed to proceed under stirring at room temperature for 3 h. After this time, the orange solution was filtered through Celite to remove a small amount of insoluble material before reducing the volume to 0.5 mL and addition of petroleum ether (10 mL) to precipitate an orange solid that was isolated by filtration and dried in vacuo. Following recrystalization from diethylether/CH_2Cl_2, a dark red powder was obtained (yield 135 mg, 84 %), m.p. 182-184

^{0}C. ^{1}H NMR (400.1 MHz, in $CDCl_3$) δ = 8.94 (d, 2H, *J* = 4.5 Hz, **H**-6), 8.36 (br, 2H, **H**C=N), 6.90-8.05 (m, 12H, protons of phenyls), 5.97 (s, 12H, protons of Ru-C_6**H**$_6$); ^{13}C NMR (100.6 MHz, in $CDCl_3$): δ = 165.47 (H**C**=N), 147.12 (**C**-6), 133.96 (**C**-13), 132.80 (d, *J* = 38.3 Hz, i-carbons of P(C_6H_6)$_2$), 132.53 (**C**-11), 131.75 (d, *J* = 12.1 Hz, *o*-carbons of P(C_6H_6)$_2$), 129.67 (s, *p*-carbons of P(C_6H_6)$_2$), 128.41 (d, *J* = 8.1 Hz, *m*-carbons of P(C_6H_6)$_2$), 124.26 (**C**-4), 122.68 (**C**-5), 119.81 (**C**-12), 117.70 (**C**-14), 161.30, 147.88, 143.12, 119.40 (quaternary carbons of phenyls), 88.12 (carbon of Ru-**C**$_6$H$_6$), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162 MHz, in $CDCl_3$): δ = 116.99 (s); IR, (KBr): ν = 906 (P-O), 1432 (P-Ph), 1619 (C=N) cm^{-1}; $C_{60}H_{48}N_4O_2P_2Ru_2Cl_4$ (mw: 1262.6 g/mol): calcd. C 57.08, H 3.83, N 4.44; found C 56.92, H 3.80, N 4.39.

4.4.2. Synthesis of [$C_{24}H_{16}N_4${NHPPh$_2$-Ru(η^6-p-cymene)Cl$_2$}$_2$], 2

To a solution of [(η^6-p-cymene)RuCl$_2$]$_2$ (77.8 mg, 0.127 mmol) in toluene, a solution (toluene, 25 mL) of (96.8 mg, 0.127 mmol) [(Ph$_2$PO)$_2$-$C_{24}H_{16}N_4$], was added. The resulting reaction mixture was allowed to proceed under stirring at room temperature for 3 h. After this time, the orange solution was filtered through Celite to remove a small amount of insoluble material before reducing the volume to 0.5 mL and addition of petroleum ether (10 mL) to precipitate an orange solid that was isolated by filtration and dried in vacuo. Following recrystallization from diethyl ether/CH_2Cl_2, a red powder was obtained (yield 152 mg, 87 %), m.p. 189-191 ^{0}C. 1H NMR (400.1 MHz, CDCl3) δ = 9.02 (d, 2H, *J* = 4.6 Hz, **H**-6), 8.24 (br, 2H, **H**C=N), 6.80-8.15 (m, 12H, protons of phenyls), 5.38 (d, 4H, *J* = 6.40 Hz, aromatic hydrogen of *p*-cymene), 5.31 (d, 4H, *J* = 6.4 Hz, aromatic hydrogen of *p*-cymene), 2.55 (m, 2H, -C**H**- of *p*-cymene), 1.71 (s, 6H, C**H**$_3$-Ph of *p*-cymene), 0.81 (d, 12H, *J* = 6.4 Hz, (C**H**$_3$)$_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 164.75 (H**C**=N), 145.97 (**C**-6), 135.75 (d, *J* = 45.5 Hz, *i*-carbons of P(C_6H_6)$_2$), 133.67 (**C**-13), 132.06 (d, *J* = 11.3 Hz, *o*-carbons of P(C_6H_6)$_2$), 132.58 (**C**-11), 131.14 (s, *p*-carbons of P(C_6H_6)$_2$), 128.11 (d, *J* = 10.0 Hz, *m*-carbons of P(C_6H_6)$_2$), 124.60 (**C**-4), 122.63 (**C**-5), 119.28 (**C**-12), 117.05 (**C**-14), 160.72, 147.99, 143.28, 119.20 (quaternary carbons of phenyls), 111.22, 96.18 (quaternary carbons of *p*-cymene), 92.58, 87.14 (aromatic carbons of *p*-cymene), 30.04 (-**C**H- of *p*-cymene), 21.18 ((**C**H$_3$)$_2$CHPh of *p*-cymene), 17.05 (CH_3Ph of *p*-cymene), assignment was based on the ^{1}H-^{13}C HETCOR and ^{1}H-^{1}H COSY spectra; ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 118.05 (s); IR, (KBr): ν = 906 (P-O), 1465 (P-Ph), 1619 (C=N) cm^{-1}. $C_{68}H_{64}N_4O_2P_2Ru_2Cl_4$ (mw: 1375.4 g/mol): calcd. C 59.38, H 4.69, N 4.07; found C 59.25, H 4.64, N 4.03.

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