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Novel neutral phosphinite bridged dinuclear ruthenium(II) arene complexes and their catalytic use in transfer hydrogenation of aromatic ketones: X-ray structure of a new Schiff base, N3,N3′-di-2-hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-diamine

Murat Aydemir[a,*], Feyyaz Durap[a], Akın Baysal[a], Nermin Meric[a], Ayşegül Buldağ[a], Bahattin Gümgüm[a], Saim Özkar[b], Leyla Tatar Yıldırım[c]

[a] Dicle University, Department of Chemistry, TR-21280 Diyarbakır, Turkey
[b] Middle East Technical University, Department of Chemistry, TR-06531 Ankara, Turkey
[c] Hacettepe University, Department of Engineering Physics, Beytepe, TR-06800 Ankara, Turkey

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ABSTRACT

A novel Schiff base N3,N3′-di-2-hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-diamine, **1** was synthesized from condensation of salicylaldehyde with 3,3′-diamino-2,2′-bipyridine. Reaction of **1** with two equivalents of PPh_2Cl in the presence of Et_3N proceeds in toluene to give N3,N3′-di-2-(diphenylphosphino)benzylidene-[2,2′]bipyridinyl-3,3′-diamine, **2** in quantitative yield. Ruthenium(II) dimers $[Ru(\eta^6\text{-arene})(\mu\text{-}Cl)Cl]_2$ readily react with phosphinite ligand $[(Ph_2PO)_2\text{-}C_{24}H_{16}N_4]$, **2** in toluene at room temperature, to afford the neutral derivatives $[C_{24}H_{16}N_4\{OPPh_2\text{–}Ru(\eta^6\text{-arene})Cl_2\}_2]$ {arene: benzene **3**, *p*-cymene, **4**}. All the complexes were fully characterized by analytical and spectroscopic methods. $^{31}P\text{–}\{^1H\}$ NMR, $^1H\text{–}^{13}C$ HETCOR or $^1H\text{–}^1H$ COSY correlation experiments were used to confirm the spectral assignments. Molecular structure of the Schiff base, **1** was also determined by X-ray single crystal diffraction study. The catalytic activity of complexes **3** and **4** in the transfer hydrogenation of acetophenone derivatives was tested. Stable ruthenium(II)–phosphinite complexes were found to be efficient catalysts in the transfer hydrogenation of aromatic ketones in excellent conversions up to 99% (up to 530 per hour) in the presence of *iso*-PrOH/KOH.

1. Introduction

One of the most challenging research areas in both material science and supramolecular chemistry is the design and synthesis of multifunctional compounds with desirable properties such as luminescence, redox, transport of information and catalytic activity [1,2]. Ligands bearing one or more chelating 2,2′-bipyridine or 1,10-phenanthroline units have attracted considerable interest as building blocks in the preparation of supramolecular architectures in combination with a wide range of transition metals [3,4]. Schiff bases are important class of ligands, and such ligands have been extensively studied in coordination chemistry mainly due to their facile synthesis and their applications in many biological aspects and in catalysis [5–7]. Schiff base ligands are most often obtained from *o*-hydroxy aromatic aldehydes (e.g. salicylaldehyde) with aliphatic or aromatic mono- or diamines. Schiff base pyridine, bipyridine, terpyridine, phenanthroline, naphtyridine and pyridine–pyridazine ligands exhibit a rich coordination chemistry towards transition metal complexes providing unusual coordination modes [8,9].

The chemistry of aminophosphines and phosphinites has also been intensively explored in recent years [10]. These compounds are extremely attractive as potential ligands since various structural modifications are accessible via simple P–N and P–O bond formation [11]. Many modified phosphine ligands and a variety of chiral aminophosphine–phosphinite ligands have important applications in organometallic chemistry and catalysis, giving selective catalysts for hydroformylation, hydrosilylation and asymmetric transfer hydrogenation [12–15]. 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 [16,17], even though some of their complexes have proved to be efficient catalysts [18,19].

Le Lagadec and co-workers [20] have reported the first crystallographic determination of a bimetallic bridged structure using

* Corresponding author.
E-mail addresses: aydemir4921@hotmail.com, aydemir@dicle.edu.tr (M. Aydemir).

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this sort of ligands. Furthermore, a related structure has been invoked by Balakrishna et al. [21] for the formation of the ruthenium complex where the ligand also serves as bridge between two metal centers, however no crystallographic evidence was presented. Another related structure has been reported by Osborn and co-workers [22], where the phosphinite ligand PONOP [C_6H_3N-2,6-$(CH_2OPPh_2)_2$] behaves as bridging ligand between two platinum centers, forming a large 20 membered diplatinamacrocycle. Most recently [23] a similar structure has been determined for a BINAP-based phosphinite ligand BINAPO, it has been noted that compounds bearing binaphtyl-based ligands bridging two metal centers are very rare. Based on these attractive studies, our research group has reported the synthesis of bridging ligands [24] and their corresponding bridged dinuclear Ru(II) complexes [$C_{10}H_6N_2\{NHPPh_2$–Ru(η^6-*p*-cymene)$Cl_2\}_2$] and [$C_{10}H_6N_2\{OPPh_2$–Ru(η^6-*p*-cymene)$Cl_2\}_2$] and their catalytic evaluation in the transfer hydrogenation of ketones [25]. Furthermore the well-known ability of (η^6-*p*-arene)Ru(II) species to act as efficient catalysts in hydrogen transfer reactions between alcohols and ketones [26,27] prompted us to study the catalytic activity of the analogous derivatives.

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 [28]. 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 [29].

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, in this paper, we report (i) the ready synthesis of a novel Schiff base N3,N3′-di-2-hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-diamine and its corresponding bridged phosphinite ligand, (ii) the synthesis and full characterization of two bridged half-sandwiches dinuclear ruthenium(II) complexes [$C_{24}H_{16}N_4\{OPPh_2$–Ru(η^6-benzene)$Cl_2\}_2$], **3** and [$C_{24}H_{16}N_4\{OPPh_2$–Ru(η^6-*p*-cymene)$Cl_2\}_2$], **4** and (iii) their subsequent application in transfer hydrogenation of the acetophenone derivatives.

2. Experimental

2.1. Materials and methods

Unless otherwise stated, all reactions were carried out under an atmosphere of argon using conventional Schlenk glassware, 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, salicylaldehyde and 2-chloro-3-nitropyridine are purchased from Fluka and were used as received. The starting materials 3,3′-diamino-2,2′-bipyridine [30,31], [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ [32,33], [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ [34] were prepared according to the 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 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 by Gallenkamp Model apparatus with open capillaries.

2.2. GC analyses

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). The GC parameters were as follows for transfer hydrogenation of ketones; 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.

2.3. Synthesis

2.3.1. Synthesis of N3,N3′-di-2-hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-diamine, **1**

Salicylaldehyde (350 mg, 2.87 mmol) was added to solution of 3,3′-diamino-2,2′-bipyridine (250 mg, 1.35 mmol) in 20 mL of methanol. The solution was heated under reflux for 10 h. On cooling to the room temperature an orange powder was precipitated out which was out collected by vacuum filtration. Recrystallization of the crude product from ethanol gave the orange crystals of the Schiff base ligand (yield 380 mg, 72%), m.p. 207.5–208.5 °C. ^{1}H NMR (400.1 MHz, in $CDCl_3$) δ = 12.10 (s, 2H, O**H**), 8.73 (d, 2H, *J* = 4.4 Hz, **H**-6), 8.50 (s, 2H, **H**C=N), 7.64 (d, 2H, *J* = 8.0 Hz, **H**-4), 7.50 (dd, 2H, *J* = 4.4 and 8.0 Hz, **H**-5), 7.32 (dd, 2H, *J* = 7.6 and 8.0 Hz, **H**-13), 7.10 (d, 2H, *J* = 7.2 Hz, **H**-11), 6.87 (d, 2H, *J* = 8.0 Hz, **H**-14), 6.82 (dd, 2H, *J* = 7.2 and 7.6 Hz, **H**-12); ^{13}C NMR (100.6 MHz, in $CDCl_3$): δ = 164.71 (H**C**=N), 148.06 (**C**-6), 133.67 (**C**-13), 132.55 (**C**-11), 125.97 (**C**-4), 124.58 (**C**-5), 119.20 (**C**-12), 117.10 (**C**-14), 160.75, 151.70, 143.49, 119.05 (quaternary carbons), assignment was based on the ^{1}H–^{13}C HETCOR and ^{1}H–^{1}H COSY spectra; IR (KBr): υ = 1622 (C=N) cm^{-1}; $C_{24}H_{18}N_4O_2$ (mw: 394.4 g/mol): calcd. C 73.08, H 4.60, N 14.20; found C 72.96, H 4.54, N 14.15.

2.3.2. Synthesis of N3,N3′-di-2-(diphenylphosphinite)benzylidene-[2,2′]bipyridinyl-3,3′-diamine, **2**

Chlorodiphenylphosphine (60 mg, 0.254 mmol) was added to a stirred solution of N3,N3′-di-2-hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-diamine, **1** (50 mg, 0.127 mmol) and triethylamine (26 mg, 0.254 mmol) in toluene (40 mL) at 0 °C with vigorous stirring. The mixture was stirred at room temperature for 4 h and the white precipitate (triethylammonium chloride) was filtered off under argon and dried in vacuo to produce a white viscous oily compound **2** (yield: 96.8 mg, 99%). ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 117.05 (s) ppm.

2.3.3. Synthesis of [$C_{24}H_{16}N_4\{OPPh_2$–Ru(η^6-benzene)$Cl_2\}_2$], **3**

To a solution of [(η^6-benzene)$RuCl_2]_2$ (63.5 mg, 0.127 mmol) in toluene, a solution (toluene, 25 mL) of [$(Ph_2PO)_2$-$C_{24}H_{16}N_4$], **2** (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 recrystallization from diethylether/CH_2Cl_2, a red powder was obtained (yield 135 mg, 84%), m.p. 182–184 °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* = 38.0 Hz, *i*-carbons of P(C_6H_5)$_2$), 132.53 (**C**-11), 131.75 (d, *J* = 12.07 Hz, *o*-carbons of P(C_6H_5)$_2$), 129.67 (s, *p*-carbons of P(C_6H_5)$_2$), 128.41 (d, *J* = 8.0 Hz, *m*-carbons of P(C_6H_5)$_2$), 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), 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 NMR (162 MHz, in $CDCl_3$): δ = 116.99 (s); IR (KBr): υ = 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.

2.3.4. Synthesis of $[C_{24}H_{16}N_4\{OPPh_2–Ru(\eta^6\text{-}p\text{-}cymene)Cl_2\}_2]$, **4**

To a solution of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (77.8 mg, 0.127 mmol) in toluene, a solution (toluene, 25 mL) of (96.8 mg, 0.127 mmol) $[(Ph_2PO)_2\text{-}C_{24}H_{16}N_4]$, **2** 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 diethylether/CH_2Cl_2, a red powder was obtained (yield 152 mg, 87%), m.p. 189–191 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$) 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 = 6.40 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 = 6.40 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 = 45.00 Hz, *i*-carbons of P(C_6H_5)$_2$), 133.67 (**C**-13), 132.06 (d, J = 11.26 Hz, *o*-carbons of P(C_6H_5)$_2$), 132.58 (**C**-11), 131.14 (s, *p*-carbons of P(C_6H_5)$_2$), 128.11 (d, J = 10.0 Hz, *m*-carbons of P(C_6H_5)$_2$), 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), 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 (**C**H$_3$Ph of *p*-cymene), 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 = 118.05 (s); IR (KBr): υ = 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.

2.4. Transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen transfer reaction: under inert atmosphere a solution of ruthenium catalyst precursors $[C_{24}H_{16}N_4\{OPPh_2–Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **3** (0.005 mmol) or $[C_{24}H_{16}N_4\{OPPh_2–Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **4** (0.005 mmol), KOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed *iso*-PrOH (5 mL) were refluxed for 15 min for **3** and **4**. After this time a sample of the reaction mixture is taken off, diluted with acetone and immediately analyzed by gas chromatography. Conversion obtained is related to the residual unreacted ketone.

2.5. X-ray diffraction structure analysis

The single crystal X-ray diffraction studies of N3,N3′-di-2-hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-diamine were carried out using Enraf-Nonius CAD-4 single X-ray diffractometer with Cu Kα (λ = 1.54184 Å) radiation. The lattice parameters and their estimated standard deviations were determined from a least-squares refinement of 25 centered reflections in the range of $21.80 \le \theta \le 43.10°$ using CAD-4 express [35]. Data reduction was carried out using X-CAD4 [36]. The structure was solved by the direct method and refined by the full-matrix least-square technique using the programs SHELXS97 and SHELXL97 [37].

Hydrogen atom (H1) of the hydroxyl group is taken from a difference Fourier map and refined, while the other hydrogen atoms were placed with $U_{iso}(H) = 1.2\,U_{eq}(C)$. For all non-hydrogen atoms anisotropic displacement parameters were refined. Results of the X-ray structure determination are presented in Tables 1 and 2 and Fig. 1.

Table 1
Crystal data and results of structure refinement for $C_{24}H_{18}N_4O_2$.

Formula	$(C_{12}H_9N_2O)_2$
Formula weight [g/mol]	394.42
Temperature [K]	293(2)
Wavelength [Å]	1.54184
Crystal system, space group	Monoclinic, *C*2/*c* (no.15)
Unit cell dimensions: [Å,°]	a = 21.004(2), b = 8.435(2), c = 12.989(4), β = 121.94(2)
Cell volume [Å^3]	1952.8(8)
Z/Calculated density [g/cm^3]	4/1.342
Absorption coefficient [mm^{-1}]	0.711
F(0 0 0)	824
Crystal size [mm]	0.4 × 0.4 × 0.4
θ-range for data collection [°]	4.96–74.22
Limiting indices	$-22 \le h \le 26$, $-10 \le k \le 0$, $-16 \le l \le 0$
Reflections collected/unique	2023/1940 [R_{int} = 0.0329]
Max. and min. transmission	0.790 and 0.752
Refinement method	Full-matrix least-squares on F^2
Data/parameters	1940/140
Goodness-of-fit on F^2	1.193
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1264, wR_2 = 0.2328
R indices (all data)	R_1 = 0.1454, wR_2 = 0.2532
Largest diff. peak and hole [e/Å^3]	1.17, −0.95

Additional material available from Cambridge Crystallographic Data Center as deposition No: CCDC 633281 comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Table 2
Selected bond lengths (Å) and bond angles (°).

N2–C9	1.342(3)	N2–C9–C9[a]	115.7(2)
O–C1	1.358(4)	N2–C10–C11	123.5(2)
N1–C7	1.279(3)	O–C1–C2	119.7(3)
N1–C8	1.407(3)	O–C1–C6	121.4(3)
N2–C10	1.325(3)	C10–N2–C9	117.2(2)
C7–C6	1.445(3)	C12–C8–N1	126.6(2)
C9–C9[a]	1.495(4)	C7–N1–C8	122.2(2)
O–H1	1.00(8)	C9–C8–N1	116.4(2)
		C8–C9–C9[a]	120.8(2)
N1–C7–C6	122.2(2)	C5–C6–C7	119.4(2)
N2–C9–C8	123.5(2)	C1–C6–C7	121.9(2)

[a] $-x, y, 1/2-z$.

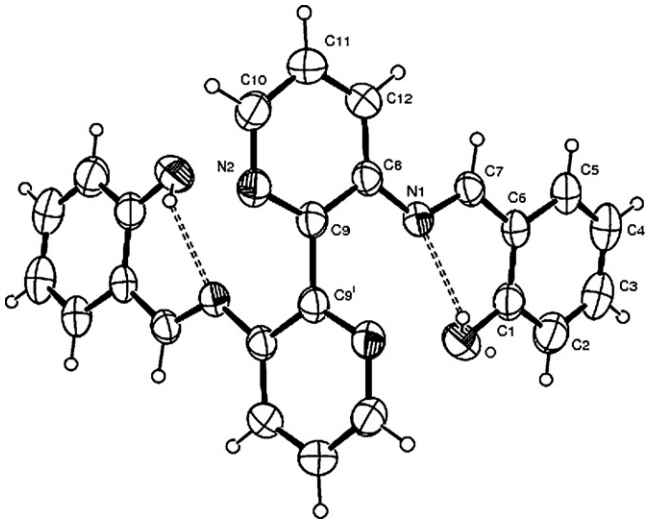
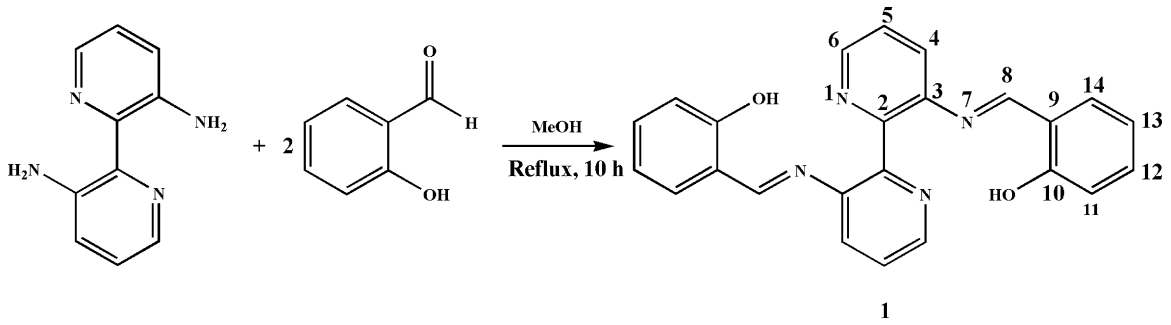


Fig. 1. Molecular structure and atomic numbering scheme of the title compound (30% probability displacement ellipsoids). H atoms are shown as small circles of arbitrary radii (i: $-x, y, -z+1/2$).



Scheme 1. Synthesis of the N3,N3′-di-2-hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-diamine, **1**.

3. Results and discussion

3.1. Synthesis of the compounds

The reaction of salicylaldehyde and 3,3′-diamino-2,2′-bipyridine in methanol yields the Schiff base N3,N3′-di-2-hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-diamine (Scheme 1). This new Schiff base was characterized by elemental analysis, IR, and multinuclear NMR spectroscopies and its structure was elucidated by X-ray crystallography.

The ^{1}H NMR spectrum of the Schiff base exhibits a characteristic signal at 8.50 ppm for the –CH=N– group and a signal at 12.07 ppm for the phenolic proton which is highly deshielded indicating an intramolecular hydrogen bonding between the phenolic OH and the imine N atom. This could be verified by structural analysis (Fig. 1). The IR spectrum also shows a broad absorption band at 3680 cm^{-1} for the O–H stretching which is broadened and shifted towards lower frequency due to the hydrogen bonding. The IR spectrum of **1** also shows a strong absorption band at 1622 cm^{-1} for the C=N stretching, indicating the presence of azomethine group.

A prismatic yellow crystal of **1** $(C_{12}H_9N_2O)_2$ was obtained from recrystallization solutions and its structure was resolved by X-ray crystallography. Fig 1 shows the molecular structure of the compound **1** with ellipsoids, 30% probability.

As a result of ongoing research program, we synthesized a novel modified bridging bidentate ligand. The reaction of the N3,N3′-di-2-hydroxybenzylidene-[2,2′]bipyridinyl-3,3′-diamine, **1** with two equivalents of chlorodiphenylphosphine in the presence of triethylamine in toluene affords phosphinite, $[(Ph_2PO)_2\text{-}C_{24}H_{16}N_4]$, **2** (Scheme 2). The ^{31}P NMR of **2** exhibits a singlet resonance due to phosphinite at 117.05 ppm in the spectrum, indicative of both phosphorus being equivalent as a result of the symmetry (C_2 symmetry) of the molecule.

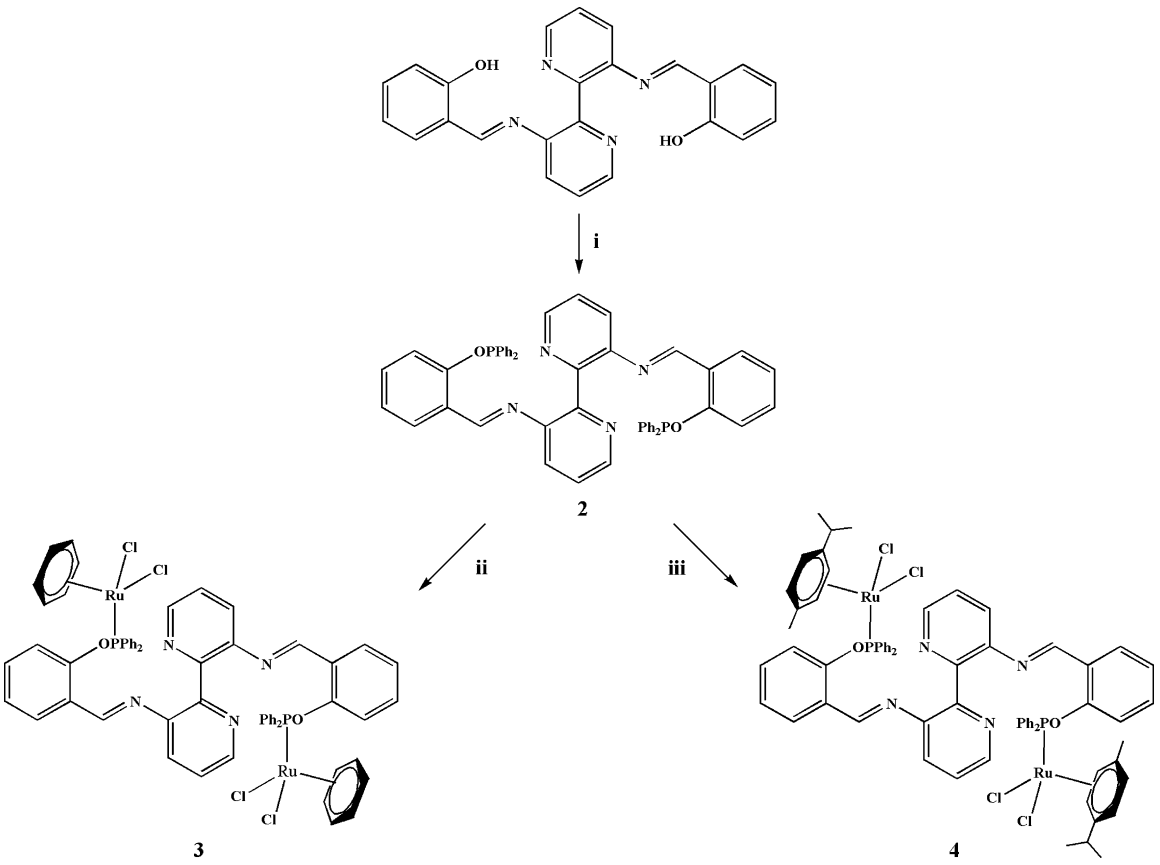
Solution of the ligand in $CDCl_3$, prepared under anaerobic condition, is unstable and decomposes gradually to give oxide and the hydrolysis product diphenylphosphinous acid, $Ph_2P(O)H$ [38,39]. Furthermore, the ^{31}P NMR spectrum also displays formation of PPh_2PPh_2 and $P(O)Ph_2PPh_2$, as indicated by signals at about δ −16.0 ppm as singlet and δ 36.8 ppm and δ −21.0 ppm as doublets with $^{1}J_{(PP)}$ 220 Hz [40]. Because the $[(Ph_2PO)_2\text{-}C_{24}H_{16}N_4]$, **2** is not stable enough in solution the ruthenium(II) complexes **3** and **4** were synthesized in situ. Reactions of $[(Ph_2PO)_2\text{-}C_{24}H_{16}N_4]$, **2** with metal precursors $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ or $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ are depicted in Scheme 2. The reaction of stoichiometric amounts of $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ and $[(Ph_2PO)_2\text{-}C_{24}H_{16}N_4]$, **2** affords the complex $[C_{24}H_{16}N_4\{OPPh_2\text{–}Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **3** in good yield as a dark red microcrystalline powder. Ligand **2** was expected to cleave the $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ dimer to give the corresponding complex **3** via monohapto coordination of the phosphinite group. Analysis by ^{31}P NMR exhibits a unique signal in the spectrum, indicative of both phosphorus being equivalent as a result of the symmetry of the complex. $[C_{24}H_{16}N_4\{OPPh_2\text{–}Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **3** was isolated as indicated by a singlet in the ^{31}P NMR spectra at (δ) 116.99 ppm, in line with the values previously observed for similar compounds [41]. It is significant to note that ^{31}P NMR signals of ligand and complex do not differ significantly [42]. Analysis by ^{1}H NMR reveals this compound to be diamagnetic, exhibiting signals corresponding to the aromatic rings for **3** at 8.05–6.90 ppm. The ^{1}H NMR spectrum of complex **3** displays the (CH=N) resonance as a broad signal at 8.36 ppm (2H) and the C_6H_6 protons as a singlet 5.97 ppm (12H). In the ^{13}C NMR spectrum of **3**, the imine carbon signal was observed at 165.47 ppm and the C_6H_6 carbon resonance was occurred at 88.12 (s) ppm. Furthermore in the ^{13}C–{^{1}H} 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 [43]. The structure of the **3** was further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values (for details see Section 2).

The reaction of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ with one equivalent of $[(Ph_2PO)_2\text{-}C_{24}H_{16}N_4]$, **2** affords only the corresponding monodendate $[C_{24}H_{16}N_4\{OPPh_2\text{–}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$ **4**, as the main product. Complexation reaction was straightforward, with coordination to ruthenium being carried out at room temperature. The initial color change, i.e. from clear orange to deep red [44], attributed to the dimer cleavage most probably by the bis(phosphinite) ligand. The ^{31}P NMR spectrum is quite consistent with the structure [45] of **4** showing a single resonance at δ 118.05 ppm. Furthermore, ^{1}H NMR spectral data of **4** is consistent with the structure proposed. The signals consisting of two doublets centered at 5.38 ppm and 5.31 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 2.55 ppm and 0.81 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 1.71 ppm.

In the ^{13}C–{^{1}H} NMR spectra of **4**, $J(^{31}P\text{–}^{13}C)$ coupling constants of the carbons of the phenyl rings were observed (for details see Section 2), which are consistent with the literature values [46–48]. The most relevant signals of ^{13}C–{^{1}H} NMR spectra of complex **4** are those corresponding to *p*-cymene ligands. Carbon atoms of the arene rings in *p*-cymene ligands are observed as two singlets at 92.58 ppm and 87.14 ppm in compound **4**. The structural composition of the complex was also confirmed by IR and elemental analysis.

3.2. Catalytic transfer hydrogenation of acetophenone derivatives

The excellent catalytic performance and the higher structural permutability of phosphinite based transition metal complexes [49–51] prompted us to develop new Ru(II) complexes with well-shaped ligands. We paid particular attention to arene ligands [52], because (i) the spectator ligands automatically occupy three



Scheme 2. Synthesis of the $[(Ph_2PO)_2\text{-}C_{24}H_{16}N_4]$, **2**, $[C_{24}H_{16}N_4\{OPPh_2\text{–}Ru(\eta^6\text{-benzene})Cl_2\}_2]$, **3** and $[C_{24}H_{16}N_4\{OPPh_2\text{–}Ru(\eta^6\text{-}p\text{-cymene})Cl_2\}_2]$, **4**. (i) 2 equiv. Ph_2PCl, 2 equiv. Et_3N, toluene, 0 °C; (ii) 1 equiv. $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, toluene, rt; (iii) 1 equiv. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$, toluene, rt.

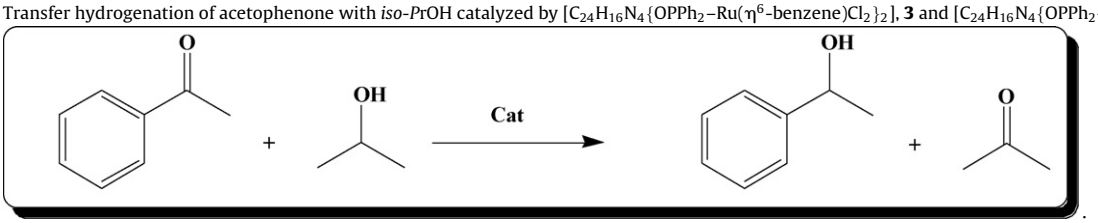
adjacent coordination sites of Ru in an octahedral coordination environment, leaving three facial sites for other functions, (ii) arene ligands that are relatively weak electron donors may provide a unique reactivity on the metallic center, and (iii) the substitution pattern on the ring is flexible. Complexes **3** and **4** were tested as catalysts in transfer hydrogenation of aromatic ketones in an *iso*-PrOH solution. *iso*-PrOH is the conventional hydrogen source having favorable properties; it is stable, easy to handle (b.p. 82 °C), non-toxic, environmentally friendly, inexpensive and many organic compounds to be catalytically reduced are soluble in it. Moreover, the acetone product is readily removable [53,54].

In a preliminary study, complexes **3** and **4** were used as precatalysts, *iso*-PrOH/KOH as the reducing system, and acetophenone as the model substrate. The results collected from the catalytic test reactions are listed in Table 3. At room temperature no appreciable formation of 1-phenylethanol was observed (Table 3, Entries 1 and 2). As can be inferred from the Table 3 (Entries 3 and 4) the precatalysts as well as the presence of KOH are necessary to observe appreciable conversions. The base facilitates the formation of ruthenium alkoxide by abstracting proton of the alcohol and subsequently alkoxide undergoes β-elimination to give ruthenium hydride, which is an active species in this reaction. This is the mechanism proposed by several workers on the studies of ruthenium-catalyzed transfer hydrogenation reaction by metal hydride intermediates [55–58]. In addition, performing the reaction in air and water slowed down the reaction but did not affect the conversion of the product. As shown in Table 3, increasing the substrate-to-catalyst ratio does not damage the conversions of the product in most cases. Remarkably, the transfer hydrogenation of acetophenone could be achieved to 99% yield even when the substrate-to-catalyst ratio reached 1000:1, though an increase in the reaction time (Table 3). However, when the reaction temperature was increased to 82 °C smooth reduction of acetophenone into 1-phenylethanol occurred, with conversion ranging from 96.5% to 97.2% after 15 min for the reaction starting with **3** and **4** (Table 4, Entries 1 and 2). A model reaction using acetophenone indicated that various structural parameters including the alkyl substituents on the arene ligands did not markedly and straightforwardly affect the rate of the reaction. The catalytic activities of **3** and **4** are measured as TOF values of 523 h^{-1} and 534 h^{-1}, respectively (Table 3, Entries 13 and 14). These values are obtained when conversion is less than 43.6% or 44.5%, respectively. Results obtained from optimization studies indicate clearly that both complexes are active and efficient catalysts leading to nearly quantitative conversions, with no significant difference between the catalytic activities.

Following the optimization studies, we also examined the transfer hydrogenations of aromatic ketones using complexes **3** and **4**. These results are presented in Table 4. The fourth column of Table 4 illustrates some conversions of the reduction performed in a 0.1 M 2-propanol solution containing **3** or **4** and KOH (ketone:Ru:KOH = 100:1:5).

The catalytic reduction of acetophenone derivatives was all tested with the conditions optimized for acetophenone. Complexes **3** and **4** showed very high activity for the 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 [59,60]. In addition, the catalytic efficiency was seen not to be dependent on the arene ligand. That is, the catalytic activity remains unaffected in the presence of free arenes. As expected, in accord with the catalytic activity shown by half-sandwich ruthenium(II) com-

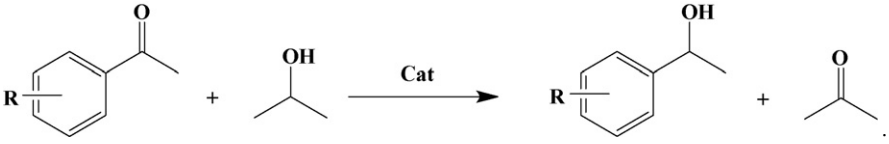
Table 3
Transfer hydrogenation of acetophenone with *iso*-PrOH catalyzed by [$C_{24}H_{16}N_4${$OPPh_2$–Ru(η^6-benzene)Cl_2}$_2$], **3** and [$C_{24}H_{16}N_4${$OPPh_2$–Ru(η^6-*p*-cymene)Cl_2}$_2$], **4**.



Entry	Catalyst	S/C/NaOH	Time	Conversion (%)[a]	TOF (h^{-1})[b]
1	**3**[c]	100:1:5	1 h	<1	–
2	**4**[c]	100:1:5	1 h	<1	–
3	**3**[d]	100:1	1 h	<5	–
4	**4**[d]	100:1	1 h	<5	–
5	**3**[e]	100:1:5	1 h	98.0	98
6	**4**[e]	100:1:5	1 h	98.3	98
7	**3**[f]	100:1:5	30 min	98.2	196
8	**4**[f]	100:1:5	30 min	99.6	199
9	**3**[g]	500:1:5	1 h	97.2	97
10	**4**[g]	500:1:5	1 h	98.3	98
11	**3**[h]	1000:1:5	3 h	96.9	32
12	**4**[h]	1000:1:5	3 h	97.8	33
13	**3**[i]	100:1:5	5 min	43.6	523
24	**4**[i]	100:1:5	5 min	44.5	534

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

Table 4
Transfer hydrogenation results for substituted acetophenones with the catalyst systems prepared from [$(Ph_2PO)_2$-$C_{24}H_{16}N_4$], **2** and [Ru(η^6-benzene)Cl_2]$_2$, **3** and [Ru(η^6-*p*-cymene)Cl_2]$_2$, **4**[a].



Entry	R	Time (min)	Conversion (%)[b]	TOF (h^{-1})[c]
[$C_{24}H_{16}N_4${$OPPh_2$–Ru(benzene)Cl_2}$_2$], 3				
1	H	15	96.5	386
2	4-F	15	99.4	398
3	4-C1	15	98.0	392
4	4-Br	15	97.2	389
5	2-MeO	15	94.6	378
6	4-MeO	15	92.8	371
[$C_{24}H_{16}N_4${$OPPh_2$–Ru(*p*-cymene)Cl_2}$_2$],4				
1	H	15	97.2	389
2	4-F	15	99.9	400
3	4-C1	15	97.5	390
4	4-Br	15	97.3	389
5	2-MeO	15	93.6	374
6	4-MeO	15	92.4	370

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*-PrOH (5 mL), KOH (0.025 mmol%), 82 °C, 15 min for **3** and **4**, the concentration of acetophenone derivatives is 0.1 M.
[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone.
[c] TOF = (mol product/mol Cat.) × h^{-1}.

plexes bearing heterodifunctional P,N-ligands [61,62], P,O-ligands [63], and NHCs ligands [64,65], complexes **3** and **4** are more active in the catalytic transfer hydrogenations of aromatic ketones leading to nearly quantitative formation of corresponding alcohols derivatives after 15 min. In regard the comparative catalytic performance with respect to analogous complexes (bridged dinuclear Ru(II)–phosphinite complexes), results indicate that the O–P linkages possibly can stabilize a catalytic transition state [66,67]. The catalytic performance shown by both of these complexes is higher than that of recently reported for the related half-sandwich complexes [68].

4. Conclusions

This report describes the preparing and characterization of two new binuclear Ru(II) complexes based monodendate phosphinite ligand and investigating their use in transfer hydrogenation of ketones. We found that these complexes are efficient homoge-

neous 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 aromatic ketones was investigated and it was seen that their catalytic activities were very similar. The procedure is simple and efficient towards various aryl ketones. Further studies of other transition metal complexes of this ligand are in progress and future investigations are aiming at the development of an asymmetric version of this catalysis.

Acknowledgements

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