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Mono- and binuclear ruthenium(II) complexes containing pyridine-2,6-diimine (Pydim) ligands: Synthesis, characterization and catalytic activity in the transfer hydrogenation of acetophenone

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Abstract

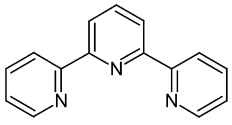
A series of neutral mono- and binuclear Ru(II) complexes: [PydimCl$_2$RuL] (Pydim (**1**) pyridine-2,6-diimine; (**2**) L = NCMe; (**3**) L = PPh$_3$) and [PydimCl$_2$Ru(L-L)RuCl$_2$Pydim] (**4**) L-L = pyrazine; (**5**) L-L = 4,4′-bipyridine) have been synthesized from the corresponding (*p*-cymene)ruthenium dichloride dimer, pydim and ancillary ligands L and L-L, respectively. The Pydim-Ru(II) complexes have been employed as catalysts for the transfer hydrogenation of acetophenone in the presence of KOH using 2-propanol as a hydrogen source. Ligand substitution studies indicate that there is a significant difference in reactivity between complexes containing L/L-L and Pydim. Yields of up to 93% were obtained after 5 min at 82 °C.

Keywords: Tridentate triamine ligands; Pyridine-2,6-diimines; Ru(II) complexes; Transfer hydrogenation of acetophenone

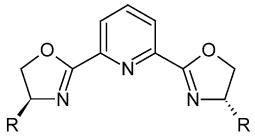
1. Introduction

Heterocyclic ligands containing nitrogen atoms are drawing a great deal of attention in coordination chemistry and homogeneous catalysis [1–3] because of the versatility of their steric and electronic properties, which can be modified by choosing the appropriate ring substituents [4].

Recently, planar tridentate pyridine-bridged *N*,*N*ĭ,*N* ligands, such as 2,2′:6,2′-terpyridines (**A**) [5], 2,6-bis(oxazolinyl) pyridines (Pybox) (**B**) [6,7]; 2,6-bis(pyrazol-1-yl)pyridine (**C**) [8] and Pydims (**D**) [9,10] have been synthesized and their Ru(II) complexes have been studied [11].



A



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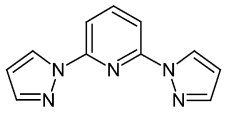

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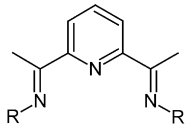

D

More recently, *trans* and *cis*-[RuCl$_2$(PPh$_3$){κ^3-*N*,*N*,*N*-(*R*,*R*)-Ph-Pybox}] have been prepared and used as highly efficient enantioselective transfer hydrogenation catalysts [12]. This report prompted us to study the catalytic activity of Ru(II) complexes with the pydims, some of which have good efficiency in the catalytic epoxydation of alkenes [9]. While the present study was in progress, a related paper on the catalytic activity of

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C in the transfer hydrogenation of aryl ketones was published [13].

We are not aware of any previous reports about transfer hydrogenation of ketones with Pydim-Ru(II) complexes. Thus, it was the goal of this work to prepare well-defined Pydim-Ru(II) catalyst precursors incorporating pydim ligands for the transfer hydrogenation of acetophenone. These complexes were found to be active catalysts for transfer hydrogenation, leading to the formation of *sec*-alcohol in high conversions.

2. Experimental

All manipulations were performed under argon using standard Schlenk Techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under argon before use. $[RuCl_2(p\text{-cymene})]_2$ [14], **1a** and **2a** [15], **1c** [9], **1d** [16], **1e** [17], **2f** [18], **1g** [19] were synthesized according to published procedures. NMR spectra were recorded at 297 K on a Varian Mercury AS 400 NMR spectrometer at 400 MHz (^{1}H), 100.56 MHz (^{13}C). The C, H and N analyses were performed using a CHNS-932 (LECO) instrument at the Technical and Scientific Research Council of Turkey, TUBITAK. Melting points were determined using an Electrothermal 9100 melting point detection apparatus and are uncorrected. IR spectra (KBr pellets) were recorded in the range 400–4000 cm^{-1} on an ATI UNICAM 2000 spectrophotometer. GC measurements for catalytic experiments were performed using an Agillent 6890N GC instrument with a HP5 capillary column.

2.1. General procedure for the synthesis of ligands

A mixture of substituted aniline (10 mL) and 2,6-diacetylpyridine (1.00 g, 6.12 mmol) was heated at 95 °C for 2 days. Then, the excess of aniline was distilled off under reduced pressure and the residue was dissolved in hot ethanol. Upon cooling to room temperature yellow crystals formed which were filtered off, washed with diethyl ether (3 × 5 mL) and dried.

2.1.1. 2,6-Bis[1-(4-fluorophenylimino)ethyl] pyridine **1b**

Yield: 1.95 g, 91%. mp 138–140 °C. ^{1}H NMR (δ, $CDCl_3$): 2.33 [s, 6H, N=C-*Me*]; 6.73 [dd, 4H, J_1 = 8.8 Hz, J_2 = 4.8 Hz, Ph-H_o]; 6.94 [dd, 4H, J_1 = 8.8 Hz, J_2 = 4.8 Hz, Ph-H_m]; 7.87 [t, 1H, J = 7.8 Hz, Py-H_p], 8.34 [d, 2H, J = 8.0 Hz, Py-H_m]. ^{13}C NMR (δ, $CDCl_3$): 16.39; 115.83; 120.99; 122.61; 137.08; 147.42; 158.62; 161.03; 168.21. IR (KBr; cm^{-1}): 1651($\nu_{C=N}$).

2.1.2. 2,6-Bis[1-(2-methyl-6-ethylphenylimino)ethyl] pyridine **1f**

Yield: 2.24 g, 92%. mp 160–161 °C. ^{1}H NMR (δ, $CDCl_3$): 1.08 [t, 6H, J = 7.6 Hz, 2-Me-6-CH_2*Me*-Ph]; 1.98 [s, 6H, 2-*Me*-6-CH_2Me-Ph]; 2.18 [s, 6H, *N*=C-*Me*]; 2.33 [m, 4H, 2-Me-6-*CH_2*Me-Ph]; 6.92 [t, 2H, J = 7.6 Hz, Ph-H_p], 7.03 [t, 4H, J = 8.6 Hz, Ph-H_m], 7.85 [t, 1H, J = 8.0 Hz, Py-H_p], 8.14 [d, 2H, J = 8.0 Hz, Py-H_m]. ^{13}C NMR (δ, $CDCl_3$): 14.06; 16.90; 18.22; 24.94; 122.52; 123.47; 125.44; 126.28; 128.16; 131.81; 137.11; 148.38; 155.33; 167.40. IR (KBr; cm^{-1}): 1640($\nu_{C=N}$).

2.2. Synthesis of complexes

2.2.1. General procedure for the synthesis of Type 2 complexes

An ethanolic solution (15 mL) of 1.10 eq. of **1** was mixed with $[RuCl_2(p\text{-cymene})]_2$ (306 mg, 0.50 mmol). The reaction mixture was heated under reflux for 10 h. The refluxing dark brown solution was cooled to room temperature. Ethanol was removed by distillation and then the residue was dissolved in dichloromethane (15 mL) containing acetonitrile (1 mL) and precipitated by addition of diethyl ether (30 mL). The microcrystalline solid was filtered off and washed with diethyl ether (3 × 10 mL) and pentane (3 × 10 mL). The desired products were dried under reduced pressure at 50 °C for 1 h.

2.2.2. {(Acetonitrile)(2,6-bis[1-(4-fluorophenylimino) ethyl]pyridine)dichlororuthenium(II)} [Ru(**1b**)(CH_3CN)Cl_2] (**2b**)

Yield: 430 mg, 77%. mp 218–220 °C. Anal. calcd. for $C_{23}H_{20}Cl_2F_2N_4Ru$: C 49.12; H 3.58; N 9.96%; found: C 49.36; H 3.77; N 9.58%. ^{1}H NMR (δ, $CDCl_3$): 2.13 [s, 3H, *Me*CN]; 2.75 [s, 6H, *N*=C-*Me*]; 7.04 [d, 4H, J = 7.8, Ph-H_m]; 7.27 [d, 4H, J = 8.0, Ph-H_o]; 7.90 [t, 1H, J = 7.8, Py-H_p], 8.03[d, 2H, J = 7.8, Py-H_m]. ^{13}C NMR (δ, $CDCl_3$): 5.85; 18.29; 113.36; 118.54; 120.93; 130.63; 141.44; 148.05; 158.22; 165.03; 171.14. IR (KBr; cm^{-1}): 1637 ($\nu_{C=N}$).

2.2.3. {(Acetonitrile)(2,6-bis[1-(2-methyl-4-N,N-diethylaminophenylimino)ethyl]pyridine) dichlororuthenium(II)} [Ru(**1d**)(CH_3CN)Cl_2] (**2d**)

Yield: 460 mg, 67%. mp 182 °C (dec.). Anal. calcd. for $C_{32}H_{42}Cl_2N_6Ru$: C 56.30; H 6.20; N 12.31%; found: C 55.96; H 6.59; N 11.92%. ^{1}H NMR (δ, $CDCl_3$): 1.14 [t, 12H, J = 7.0 Hz, 2-Me-4-N(CH_2*Me*)$_2$-Ph]; 2.05 [s, 3H, *Me*CN]; 2.18 [s, 6H, 2-*Me*-4-N(CH_2Me)$_2$-Ph]; 2.63 [s, 6H, *N*=C-*Me*]; 3.32 [q, 8H, J_1 = 14 Hz, J_2 = 6.4, 2-Me-4-N(*CH_2*Me)$_2$-Ph]; 6.50 [br, 4H, Ph-H_m]; 7.41 [d, 2H, J = 8.4, Ph-H_o]; 7.51 [t, 1H, J = 8.0 Hz, Py-H_o], 7.72 [d, 2H, J = 8.0 Hz, Py-H_m]. ^{13}C NMR (δ, $CDCl_3$): 0.21; 8.85; 13.70; 15.73; 40.74; 106.09; 109.63; 118.22; 120.74; 121.96; 123.92; 126.63; 135.49; 142.17; 159.60; 166.71. IR (KBr; cm^{-1}): 1596 ($\nu_{C=N}$).

2.2.4. {(Acetonitrile)(2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine)dichlororuthenium(II)} [Ru(**1e**)(CH_3CN)Cl_2] (**2e**)

Yield: 450 mg, 74%. mp 130 °C (dec.). Anal. calcd. for $C_{29}H_{34}Cl_2N_4Ru$: C 57.05; H 5.61; N 9.18%; found: C 56.96; H 5.93; N 9.24%. ^{1}H NMR (δ, $CDCl_3$): 2.23 [s, 12H, 2,6-(*Me*)$_2$-4-Me-Ph]; 2.24 [s, 3H, *Me*CN]; 2.26 [s, 6H, 2,6-(Me)$_2$-4-*Me*-Ph]; 2.60 [s, 6H, *N*=C-*Me*]; 6.84 [s, 4H, Ph-H_m]; 7.56 [t, 1H, J = 8.0 Hz, Py-H_p], 7.81 [d, 2H, J = 8.4 Hz, Py-H_m]. ^{13}C NMR (δ, $CDCl_3$): 4.97; 18.51; 21.12; 123.79; 127.50; 128.24; 129.43; 131.88; 135.45; 145.68; 163.47; 172.99. IR (KBr; cm^{-1}): 1605($\nu_{C=N}$).

*2.2.5. {(Acetonitrile)(2,6-bis[1-(phenylimino)ethyl] pyridine)dichlororuthenium(II)} [Ru(**1g**)(CH_3CN)Cl_2] (**2g**)*

Yield: 405 mg, 77%. mp 217–219 °C. Anal. calcd. for $C_{23}H_{22}Cl_2N_4Ru$: C 52.48; H 4.21; N 10.64%; found: C 52.58; H 4.76; N 10.34%. ^{1}H NMR (δ, $CDCl_3$): 1.96 [s, 3H, *Me*CN]; 2.72 [s, 6H, N=C-*Me*]; 6.94 [d, 4H, J = 7.2, Ph-H_o]; 7.05-7.21 [m, 6H, Ph-$H_{m\text{-}p}$] 7.65 [t, 1H, J = 8.0, Py-H_p]; 7.88 [d, 2H, J = 8.4 Hz, Py-H_m]. ^{13}C NMR (δ, $CDCl_3$): 5.43; 16.34; 121.51; 127.92; 130.37; 135.13; 137.71; 145.13; 151.91; 156.35; 163.22. IR(KBr; cm^{-1}): 1639 ($\nu_{C=N}$).

2.3. General procedure for the synthesis of Type 3 complexes

An ethanolic solution (15 mL) of 1.10 eq. of **1** was mixed with [$RuCl_2$(*p*-cymene)]$_2$ (306 mg, 0.50 mmol). The reaction mixture was heated under reflux for 10 h. The resulting dark brown solution was cooled to room temperature and PPh_3 (262 mg, 1 mmol) was added. The mixture was heated under reflux for a further 2 h. The volatiles were removed under reduced pressure and then the residue was dissolved in dichloromethane (15 mL) and precipitated by addition of diethyl ether (30 mL). The microcrystalline solid was filtered off and washed with diethyl ether (3 × 10 mL) and pentane (3 × 10 mL). The desired products were dried under reduced pressure at 50 °C for 1 h.

*2.3.1. {(2,6-Bis[1-(4-N,N-dimethylaminophenylimino) ethyl]pyridine)(triphenylphosphine) dichlororuthenium(II)} [Ru(**1a**)(PPh_3)Cl_2] (**3a**)*

Yield: 514 mg, 62%. mp > 350 °C. Anal. calcd. for $C_{43}H_{44}Cl_2N_5PRu$: C 61.94; H 5.32; N 8.40%; found: C 61.13; H 4.93; N 7.95%. ^{1}H NMR (δ, $CDCl_3$): 2.34 [s, 6H, N=C-*Me*]; 2.97 [s, 12H, 4-N(*Me*)$_2$-Ph]; 6.48-6-53 [br, 8H, Ph-*H*]; 6.85 [t, 3H, J = 7.2 Hz, PPh_3-H_m]; 7.08 [t, 6H, J = 7.2 Hz, PPh_3-H_p]; 7.18 [t, 6H, J = 8.0 Hz, PPh_3-H_o]; 7.28 [d, 2H, J = 7.8 Hz, Py-H_m]; 7.35 [t, 1H, J = 7.8 Hz, Py-H_p].^{13}C NMR (δ, $CDCl_3$): 18.46; 40.96; 111.08; 112.35; 123.55; 127.85; 128.74; 133.11; 135.39; 137.98; 148.64; 149.57; 163.56, 169.27. IR (KBr; cm^{-1}): 1617($\nu_{C=N}$).

*2.3.2. {(2,6-Bis[1-(4-fluorophenylimino)ethyl]pyridine} (triphenylphosphine) dichlororuthenium(II)} [Ru(**1b**)(PPh_3)Cl_2] (**3b**)*

Yield: 630 mg, 80%. mp > 350 °C. Anal. calcd. for $C_{39}H_{32}Cl_2F_2N_3PRu$: C 59.77; H 4.12; N 5.36%; found: C 59.95; H 4.23; N 5.04%. ^{1}H NMR (δ, $CDCl_3$): 2.30 [s, 6H, N=C-*Me*]; 6.86 [t, 4H, J = 8.0, Ph-H_m]; 7.06–7.20 [m, 19H, PPh_3-*H* and Ph-H_o]; 7.24[t, 1H, J = 7.8, Py-H_p]; 7.37 [d, 2H, J = 7.8, Py-H_m]. ^{13}C NMR (δ, $CDCl_3$): 17.33; 118.44; 121.74; 125.82; 129.46; 133.65; 134.15; 138.04; 139.91; 145.61; 157.67; 162.13; 170.32. IR (KBr; cm^{-1}): 1635 ($\nu_{C=N}$).

*2.3.3. 2,6-Bis[1-(2-methyl-4-N,N-diethylaminophenylimino)ethyl]pyridine(triphenylphosphine) dichlororuthenium(II)} [Ru(**1d**)(PPh_3)Cl_2] (**3d**)*

Yield: 610 mg, 66%. mp > 350 °C. *Anal*. calcd. for $C_{49}H_{56}Cl_2N_5PRu$: C 64.11; H 6.15; N 7.63%; found: C 61.13; H 4.93; N 7.95%. ^{1}H NMR (δ, $CDCl_3$): 1.28 [t, 12H, J = 7.4 Hz, 2-Me,4-N(CH_2-*Me*)$_2$-Ph]; 2.47 [s, 6H, 2-*Me*,4-N(CH_2Me)$_2$Ph]; 3.34 [s, 6H, N=C-*Me*]; 3.72 [m, 8H, 2-Me,4-N(*CH_2*Me)$_2$Ph]; 6.89 [br, 6H, Ph-*H*]; 7.22[t, 6H,J = 7.6, PPh_3-H_m]; 7.49 [t, 6H, J = 7.6 PPh_3-H_p]; 7.72 [t, 1H, J = 7.8, Py-H_p] 7.81 [t, 6H, J = 7.6, PPh_3-H_o]; 8.67 [d, 2H, J = 8.0, Py-H_m] ^{13}C NMR (δ, $CDCl_3$): 10.78; 14.12; 16.75; 42.33; 112.37; 113.80; 115.12; 119.38; 122.43; 124.13; 128.44; 130.27; 132.74; 133.48; 138.53; 145.64; 157.12; 165.73. IR (KBr; cm^{-1}): 1602($\nu_{C=N}$).

2.4. General procedure for the synthesis of Type 4 complexes

An ethanolic solution (15 mL) of 1.10 eq. of **1** was mixed with [$RuCl_2$(*p*-cymene)]$_2$ (306 mg, 0.50 mmol). The reaction mixture was heated under reflux for 10 h. The resulting dark brown solution was cooled to room temperature and pyrazine (40 mg, 0.50 mmol) was added. The mixture was heated under reflux for a further 2 h. The volatiles were removed under reduced pressure and then the residue was dissolved in dichloromethane (15 mL) and precipitated by addition of diethyl ether (30 mL). The microcrystalline solid was filtered off and washed with diethyl ether (3 × 10 mL) and pentane (3 × 10 mL). The desired products were dried under reduced pressure at 50 °C for 1 h.

*2.4.1. {(μ-Pyrazine)bis-[{2,6-bis[1-(4-N,N-methylaminophenylimino)ethyl]pyridine} dichlorodiruthenium(II)]} [Ru_2(**1a**)$_2Cl_4$($C_4H_4N_2$)] (**4a**)*

Yield: 400 mg, 65%. mp = 323 °C (dec.). Anal. calcd. for $C_{60}H_{66}Cl_4N_{12}Ru_2$: C 53.03; H 5.11; N 13.74%; found: C 53.12; H 5.87; N 13.96%. ^{1}H NMR (δ, $CDCl_3$): 2.78 [s, 12H, N=C-*Me*]; 2.86 [s, 12H, 4-N*Me*$_2$-Ph]; 2.89 [s, 12H, 4-N*Me*$_2$-Ph]; 6.49 [d, 8H, J = 8.0 Hz, Ph-H_m]; 6.89 [d, 8H, J = 7.8 Hz, Ph-H_o]; 7.59 [t, 2H, J = 7.4 Hz, Ph-H_p]; 7.80 [d, 4H, J = 7.8 Hz, Py-H_m]; 7.94 [d, 4H, J = 4.3 Hz, Pyz-*H*]. ^{13}C NMR (δ, $CDCl_3$): 18.17; 40.96; 112.85; 122.86; 124.15; 124.60; 144.16; 148.77; 150.85; 163.44; 170.06. IR (KBr; cm^{-1}): 1605($\nu_{C=N}$).

*2.4.2. {(μ-Pyrazine)bis-[{2,6-bis[1-(4-fluorophenylimino)ethyl]pyridine}dichloro diruthenium(II)]} [Ru_2(**1b**)$_2Cl_4$($C_4H_4N_2$)] (**4b**)*

Yield: 480 mg, 86%. mp > 350 °C. Anal. calcd. for $C_{46}H_{38}Cl_4F_4N_8Ru_2$: C 49.21; H 3.41; N 9.98%; found: C 49.55; H 3.76; N 9.66%. ^{1}H NMR (δ, $CDCl_3$): 2.77 [s, 12H, N=C-*Me*]; 6.87–7.11 [m, 16H, Ph-*H*]; 7.68 [t, 2H, J = 7.8, Py-H_p]; 7.91 [d, 4H, J = 8.0, *Py*-H_m]; 8.02 [d, 1H, J = 4.8, Pyz-*H*]; 8.21 [d, 1H, J = 4.8, Pyz-*H*]; 8.42 [d, 1H, J = 5.6, Pyz-*H*]; 8.71 [d, 1H, J = 5.2, Pyz-*H*]. ^{13}C NMR (δ, $CDCl_3$): 19.12; 121.93; 126.09; 128.13; 129.30; 146.26; 147.73; 150.60; 163.56; 171.67. IR (KBr; cm^{-1}): 1613($\nu_{C=N}$).

*2.4.3. {(μ-Pyrazine)bis-[{2,6-bis[1-(4-tert-buthylphenylimino)ethyl]pyridine} dichlorodiruthenium(II)]} [Ru_2(**1c**)$_2Cl_4$($C_4H_4N_2$)] (**4c**)*

Yield: 510 mg, 80%. mp > 350 °C. Anal. calcd. for $C_{62}H_{74}Cl_4N_8Ru_2$: C 58.39; H 5.85; N 8.79%; found: C 57.92;

H 5.67; N 9.86%. IR (KBr; cm^{-1}): 1576 ($\nu_{C=N}$). ^1H NMR (δ, $CDCl_3$): 1.27 [s, 36H, 4-C(*Me*)$_3$Ph]; 2.75 [s, 6H, N=C-*Me*]; 2.78 [s, 6H, N=C-*Me*]; 6.88 [d, 4H, J = 8.4 Hz, Ph-H_m]; 6.94 [d, 4H, J = 8.4 Hz, Ph-H_m]; 7.20 [d, 4H, J = 8.4 Hz, Ph-H_o]; 7.25 [d, 4H, J = 8.8 Hz, Ph-H_o]; 7.58 [t, 2H, J = 8.0 Hz, Py-H_p]; 7.82 [d, 4H, J = 8.8 Hz, Py-H_m]; 7.89 [s, 4H, Pyz-*H*]. ^{13}C NMR (δ, $CDCl_3$): 18.02; 31.55; 34.77; 122.26; 125.75; 128.44; 129.25; 146.02; 147.48; 149.97; 162.35; 170.61. IR (KBr; cm^{-1}): 1576($\nu_{C=N}$).

2.4.4. {(μ-Pyrazine)bis-[{2,6-bis[1-(2-methyl-4-N,N-diethylaminophenylimino)ethyl]pyridine} dichlorodiruthenium(II)]} [Ru_2(**1d**)$_2Cl_4(C_4H_4N_2)$] (**4d**)

Yield: 940 mg, 68%. mp 355 °C (dec.). Anal. calcd. for $C_{66}H_{86}Cl_4N_{12}Ru_2$: C 56.97; H 6.23; N 12.08%; found: C 56.20; H 6.32; N 11.92%. ^1H NMR (δ, $CDCl_3$): 0.95–1.11 [m, 24H, 2-Me,4-N(CH_2-*Me*)$_2$-Ph]; 1.76–2.09 [m, 12H, 2-*Me*,4-N(CH_2-Me)$_2$-Ph]; 2.65 [d, 12H, J = 5.6 Hz, N=C-*Me*]; 2.97–3.31 [m, 16H, 2-Me,4-N(*CH*$_2$-Me)$_2$-Ph]; 6.06-6.18 [m, 4H, Ph-H_m]; 6.27–6.34 [m, 4H, Ph-H_m]; 6.68–6.86 [m, 4H, Ph-H_o]; 7.45–7.64 [m, 6H, Py-*H*]; 7.70–7.74 [m, 4H, Pyz-*H*]. ^{13}C NMR (δ, $CDCl_3$): 12.77; 15.98; 18.31; 44.34; 109.63; 115.11; 117.64; 121.31; 129.00; 135.46; 138.72; 145.78; 148.36; 158.97; 170.31. IR (KBr; cm^{-1}): 1583 ($\nu_{C=N}$).

2.4.5. {(μ-Pyrazine)bis-[{2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine}dichloro diruthenium(II)]} [Ru_2(**1e**)$_2Cl_4(C_4H_4N_2)$] (**4e**)

Yield 457 mg, 75%. mp 182 °C (dec.). Anal. calcd. for $C_{58}H_{66}Cl_4N_8Ru_2$: C 57.14; H 5.46; N 9.19%. found: C 56.78; H 6.32; N 10.18%. ^1H NMR (δ, $CDCl_3$): 2.01 [s, 24H, 2,6-(*Me*)$_2$,4-Me-Ph]; 2.13 [s, 12H, 2,6-(Me)$_2$,4-*Me*-Ph]; 2.63 [s, 12H, N=C-*Me*]; 6.59 [s, 8H, Ph-*H*]; 7.67 [t, 2H, J = 7.8 Hz, Py-H_p]; 7.89 [d, 4H, J = 8.0 Hz, Py-H_m]; 8.24 [s, 4H, Pyz-*H*]. ^{13}C NMR (δ, $CDCl_3$): 18.34; 20.54; 123.57; 128.51, 129.33, 131.36, 135.50; 144.60; 147.76; 162.26, 173.49. IR (KBr; cm^{-1}): 1635($\nu_{C=N}$).

2.4.6. {(μ-Pyrazine)bis-[{2,6-bis[1-(2-methyl-6-ethylphenylimino)ethyl]pyridine}dichloro diruthenium(II)]} [Ru_2(**1f**)$_2Cl_4(C_4H_4N_2)$] (**4f**)

Yield 515 mg, 84%. mp 389 °C (dec.). Anal. calcd. for $C_{58}H_{66}Cl_4N_8Ru_2$: C 57.14; H 5.46; N 9.19%; found: C 57.88; H 4.96; N 9.67%. ^1H NMR (δ, $CDCl_3$): 0.86–1.01 [m, 12H, 2-Me-6-(CH$_2$-*Me*)-Ph]; 2.03–2.18 [m, 12H, 2-*Me*-6-(CH$_2$-Me)-Ph]; 2.53–2.69 [m, 16H, 2-Me-6-(*CH*$_2$-Me)-Ph]; 2.63 [s, 12H, N=C-*Me*]; 6.76-6.95 [m, 12H, Ph-*H*]; 7.70 [t, 2H, J = 8.2 Hz, Py-H_p]; 7.91 [d, 4H, J = 8.0 Hz, Py-H_m]; 8.24–8.30 [m, 4H, Pyz-*H*]. ^{13}C NMR (δ, $CDCl_3$): 15.62; 18.83; 20.85; 25.14; 123.74, 126.65, 127.02; 128.73; 131.18; 137.48; 138.17; 146.06; 147.84; 162.35; 173.71. IR (KBr; cm^{-1}): 1619($\nu_{C=N}$).

2.5. General procedure for the synthesis of Type 5 complexes

An ethanolic solution (15 mL) of 1.10 eq. of **1** was mixed with $[RuCl_2(p\text{-cymene})]_2$ (306 mg, 0.50 mmol). The reaction mixture was heated under reflux for 10 h. The resulting dark brown solution was cooled to room temperature and 4,4′-bipyridine (40 mg, 0.50 mmol) was added. The mixture was heated under reflux for a further 2 h. The volatiles were removed under reduced pressure and then the residue was dissolved in dichloromethane (15 mL) and precipitated by addition of diethyl ether (30 mL). The microcrystalline solid was filtered off and washed with diethyl ether (3 × 10 mL) and pentane (3 × 10 mL). The desired products were dried under reduced pressure at 50 °C for 1 h.

2.5.1. {(μ-4,4ĭ-Bipyridine)bis-[{2,6-bis[1-(4-N,N-methylaminophenylimino)ethyl]pyridine} dichloro diruthenium(II)]} [Ru_2(**1a**)$_2Cl_4(C_{10}H_8N_2)$] (**5a**)

Yield: 420 mg, 68%. mp 368 °C (dec.). Anal. calcd. for $C_{60}H_{66}Cl_4N_{12}Ru_2$: C 55.47; H 5.12; N 12.94%; found: C 55.12; H 5.05; N 13.11%. ^1H NMR (δ, $CDCl_3$):): 2.77 [s, 12H, N=C-*Me*]; 2.84 [s, 24H, 4-N*Me*$_2$-Ph]; 6.46 [d, 8H, J = 8.4 Hz, Ph-H_m]; 6.90–6.93 [m, 12H, Ph-H_o, Bpy-H_m]; 7.54 [t, 2H, J = 7.8 Hz, Py-H_p]; 7.81 [d, 4H, J = 8.4 Hz, Py-H_m]; 8.55 [d, 4H, J = 5.3 Hz, Bpy-H_o]. ^{13}C NMR (δ, $CDCl_3$): 17.89; 40.98; 112.53; 123.70; 127.67; 134.54; 139.56; 143.20; 149.09; 155.72; 163.43; 173.84. IR (KBr; cm^{-1}): 1609 ($\nu_{C=N}$).

2.5.2. {(μ-4,4ĭ-Bipyridine)bis-[{2,6-bis[1-(2-methyl-4-N,N-diethylaminophenylimino)ethyl] pyridine} dichlorodiruthenium(II)]} [Ru_2(**1d**)$_2Cl_4(C_{10}H_8N_2)$] (**5d**)

Yield: 510 mg, 70%. mp 330 °C (dec.). Anal. calcd. for $C_{72}H_{90}Cl_4N_{12}Ru_2$: C 58.93 H 6.18; N 11.45%; found: C 59.10; H 6.11; N 11.41%. ^1H NMR (δ, $CDCl_3$): 1.04 [t, 24H, J = 6.6 Hz, 2-Me,4-N(CH_2-*Me*)$_2$-Ph]; 2.19 [s, 12H, 2-*Me*,4-N(CH_2-Me)$_2$-Ph]; 2.73 [s, 12H, N=C-*Me*]; 3.18–3.30 [m, 16H, 2-Me,4-N(*CH*$_2$-Me)$_2$-Ph]; 6.17 [d, 4H, J = 8.8 Hz, Ph-H_o]; 6.45 [s, 4H, Ph-H_m]; 6.86 [d, 4H, J = 6.4 Hz, Bpy-H_m]; 6.93 [t, 4H, J = 8.2 Hz, Ph-H_m]; 7.59 [t, 2 H, J = 8.0 Hz, Py-H_p]; 7.84 [d, 4H, J = 8.0, Py-H_m]; 8.55 [d, 4H, J = 4.8, Bpy-H_o]. ^{13}C NMR (δ, $CDCl_3$): 12.63; 16.01; 18.34; 45.94; 110.56; 115.49; 118.67; 120.21; 121.72; 129.96; 136.54; 140.01; 144.32; 146.16; 155.22; 162.42; 172.12. IR (KBr; cm^{-1}): 1600($\nu_{C=N}$).

2.5.3. {(μ-4,4ĭ-Bipyridine)bis-[{2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine} dichlorodiruthenium(II)]} [Ru_2(**1e**)$_2Cl_4(C_{10}H_8N_2)$] (**5e**)

Yield: 526 mg, 81%. mp 260 °C (dec.). Anal. calcd. for $C_{64}H_{70}Cl_4N_8Ru_2$: C 59.35; H 5.45; N 8.65%. found: C 59.87; H 4.92; N 8.94%. ^1H NMR (δ, $CDCl_3$): 2.04 [s, 24H, 2,6-(*Me*)$_2$,4-Me-Ph]; 2.25 [s, 12H, 2,6-(Me)$_2$,4-*Me*-Ph]; 2.68 [s, 12H, N=C-*Me*]; 6.76 [s, 8H, Ph-*H*]; 7.05 [d, 4H, J = 6.0, Bpy-H_m]; 7.69 [t, 2H, J = 7.8 Hz, Py-H_p]; 7.93 [d, 4H, J = 8.0 Hz, Py-H_m]; 8.52 [d, 4H, J = 6.0, Bpy-H_o]. ^{13}C NMR (δ, $CDCl_3$): 18.74; 20.92; 119.76; 123.70; 127.78; 129.42; 132.12; 135.36; 143.60; 144.63; 155.52; 162.97; 173.70. IR (KBr; cm^{-1}): 1631($\nu_{C=N}$).

2.5.4. {(μ-4,4ĭ-Bipyridine)bis-[{2,6-bis[1-(2-methyl-6-ethylphenylimino)ethyl]pyridine} dichlorodiruthenium(II)]} [Ru_2(**1f**)$_2Cl_4(C_{10}H_8N_2)$] (5**f**)

Yield 503 mg, 78%. mp 370 °C (dec.). Anal. calcd. for $C_{64}H_{70}Cl_4N_8Ru_2$: C 59.35; H 5.45; N 8.65%; found: C 60.14;

H 5.23; N 8.87%. ^{1}H NMR (δ, $CDCl_3$): 0.68–0.92 [m, 12H, 2-Me,6-(CH_2-*Me*)-Ph]; 1.99–2.16 [m, 12H, 2-*Me*-6-(CH_2-Me)-Ph]; 2.28–2.53 [m, 8H, 2-Me,6-(*CH_2*-Me)-Ph]; 2.64 [d, 12H, J = 5.2, N=C-*Me*]; 6.82–7.04 [m, 16H, Ph-*H*, Bpy-H_m]; 7.65 [t, 2H, J = 8.0 Hz, Py-H_p]; 7.89 [d, 4H, J = 8.0 Hz, Py-H_m]; 8.32–8.38 [m, 4H, Bpy-H_o]. ^{13}C NMR (δ,$CDCl_3$): 14.53; 19.34; 21.25; 25.86; 119.56; 123.04; 126.08; 127.48; 129.87; 133.23; 134.84; 146.29; 148.09; 155.53; 161.32; 168.30; 176.50. IR (KBr; cm^{-1}): 1625 ($\nu_{C=N}$).

2.6. Synthesis of μ-(pyrazine)tetrachlorobis (p-cymene)diruthenium(II), 6

A solution of pyrazine (1.00 mmol, 80 mg) in ethanol (10 mL) was added dropwise to a solution of $[RuCl_2(p\text{-cymene})]_2$ (1.00 mmol, 612 mg) in ethanol (40 mL). A yellow precipitate formed immediately. The mixture was heated under reflux for 2 h and then cooled to room temperature. A yellow precipitate was filtered off, washed with diethyl ether (3 × 10 mL) and dried under reduced pressure. Yield 600 mg, 86%; mp 228–230 °C (dec.). Anal. calcd. for $C_{24}H_{32}Cl_4N_2Ru_2$: C 41.63; H 4.66; N 4.05%; found: C 41.37; H 4.55; N 4.13%.

^{1}H NMR (δ, $CDCl_3$): 1.28 [d, 12H, J = 6.4 Hz, Me-Ph-CH(*Me*)$_2$]; 2.13 [s, 6H, *Me*-Ph-CH-(Me)$_2$]; 3.03 [m, 2H, Me-Ph-*CH*(Me)$_2$]; 5.31 [d, 4H, J = 6.0, Ph-*H*]; 5.47 [d, 4H, J = 6.0, Ph-*H*]; 8.21 [s, 4H, Pyz-*H*]. ^{13}C NMR (δ, $CDCl_3$): 17.13; 26.19; 38.26; 119.21; 123.49; 125.54; 136.78; 139.44.

2.7. Synthesis of μ-(4,4ĭ-bipyridine)tetrachlorobis (p-cymene)diruthenium(II), 7

This compound was prepared in the same manner as **6** using 4,4′-bipyridine (156 mg, 1.00 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (612 mg, 1.00 mmol)). A yellow microcrystalline solid was obtained. Yield: 720 mg, 93%. mp 244–246 °C (dec.). Anal. calcd. for $C_{30}H_{36}Cl_4N_2Ru_2$: C 46.88; H 4.72; N 3.64%; found: C 46.97; H 4.59; N 3.72%.

^{1}H NMR (δ, $CDCl_3$): 1.32 [d, 12H, J = 6.4 Hz, Me-Ph-CH(*Me*)$_2$]; 2.08 [s, 6H, *Me*-Ph-CH(Me)$_2$]; 2.99 [m, 2H, Me-Ph-*CH*(Me)$_2$]; 5.27 [d, 4H, J = 5.6, Ph-*H*]; 5.49 [d, 4H, J = 6.0, Ph-*H*]; 7.05 [d, 4H, J = 4.8, Bpy-H_m]; 9.03 [d, 4H, J = 5.2, Bpy-H_o]. ^{13}C NMR (δ, $CDCl_3$): 16.79; 27.87; 35.41; 114.56; 120.36; 128.68; 131.47; 137.46; 149.45; 153.31.

2.8. General method for transfer hydrogenation of acetophenone using Ru(II)-pydim complexes as pre-catalyst

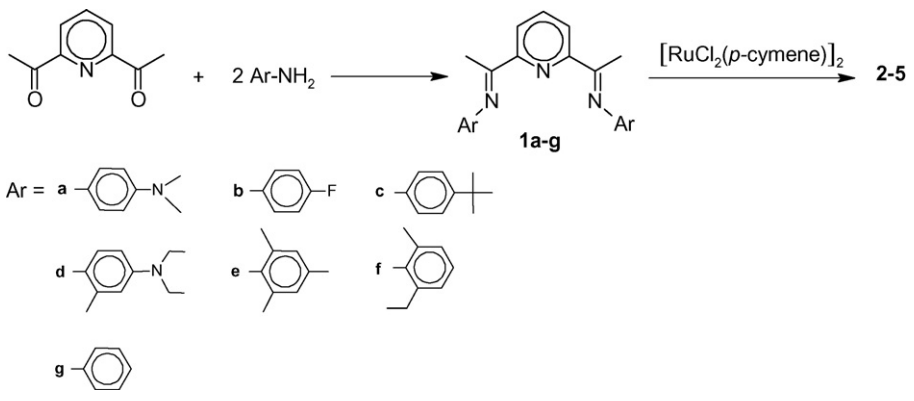
A mixture of acetophenone (10 mmol), the catalyst (0.01 mmol Ru(II)) and propan-2-ol (19 mL) were stirred at 82 °C for 10 min. 1 mL of 0.1 M KOH (0.1 mmol) solution in 2-propanol was then introduced. The mixture was stirred at refluxing temperature and the reaction was monitored by GC. After the reaction had been heated for the appropriate time, the mixture was concentrated and subjected to flash column chromatography on silica gel (CH_2Cl_2/MeOH 9:1) to afford the alcohol product. The solvent was removed under reduced pressure to give an oily residue. The identity of the products were confirmed by ^{1}H NMR spectroscopy.

3. Results and discussion

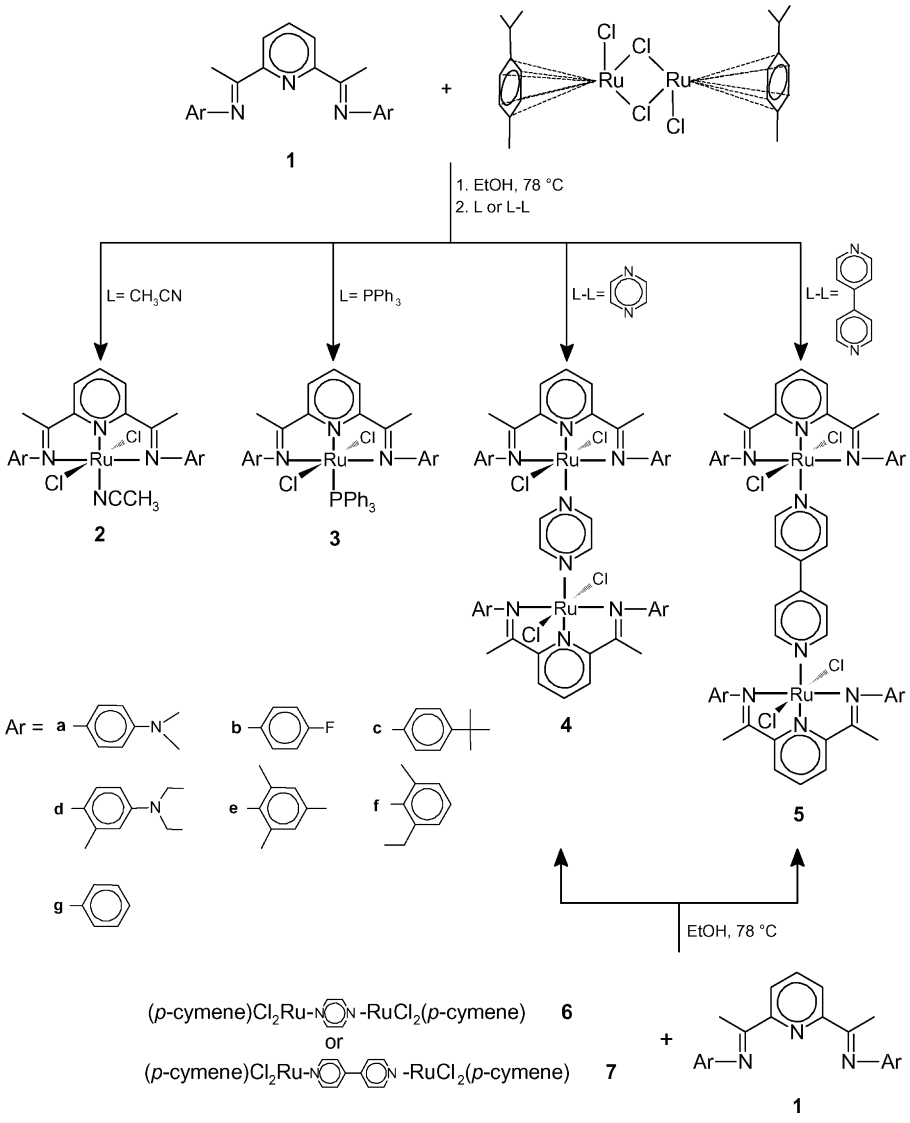
3.1. Synthesis of ligands

Pydim ligands (**1a**–**g**) were prepared in good yield by a Schiff-base condensation reaction (Scheme 1). The preparation of ligands **1a**, **c**, **d**, **e**, **g** have been described elsewhere [9,15–17,19]. All compounds were characterized by NMR and IR spectroscopy.

All the ligands gave ^{1}H and ^{13}C NMR spectra corresponding to the proposed formulations. The Py-H_p and -H_m protons were observed as doublets and triplets in a 2:1 ratio at around δ 7.75–8.48 ppm. The most notable observation in the ^{1}H NMR spectra of the free pydim ligands was that Py-H_m was more sensitive to the *p*-substituent of the aryl ring. Thus, Py-H_m signals moved further downfield as the electron withdrawing property of the *p*-substituent increased. In the ^{13}C NMR spectra, the pydim ligands exhibited a singlet at about 166–168 ppm, which can be assigned to the imine (C=N) carbon. The pydim ligands also showed a singlet at 16–17 ppm, which could be ascribed to the methyl groups in the backbone of the ligand.



Scheme 1. Synthesis of the Pydim ligands.



Scheme 2. Synthesis of mono- or binuclear Pydim-Ru(II) complexes.

3.2. Synthesis of complexes

$[Ru_2(p\text{-cymene})_2Cl_4]$ reacts with pydim ligands (**1**) in refluxing EtOH and the resulting air-stable six coordinated mono- or binuclear complexes can be isolated if the ancillary ligand (L or L-L) is added to the mixture towards the end of reaction (Scheme 2). The binuclear complexes **4** and **5** could also be prepared by reaction of the binuclear precursor complexes **6** and **7** with the appropriate pydim ligands (Scheme 2, the lower part). All of the complexes were soluble in chlorinated solvents and were fully characterized by elemental analysis and spectroscopic methods.

The ^{1}H NMR spectra of these complexes showed some differences from their respective ligands, especially in the pyridine backbone. The chemical shift of the methyl groups in the pydim backbone (complexes **3**, **4** and **5**) were singlets which had shifted towards higher field in the complexes as compared to the free ligands. In the case of type **2**, the methyl protons showed a lower chemical shift than the free pydim ligands. Similarly, Py-H_o and –H_m protons for all Pydim-Ru(II) complexes were observed as doublets and triplets in a 2:1 ratio which had shifted towards higher fields when compared to their respective free ligands except for **2b**, **3d** and **4d**. Py-H_p for **2b** and Py-H_m for **3d** showed a lower chemical shift than the free pydim ligands. Py-H_p and Py-H_m for **4d** were observed as multiplets. The stereochemistry was determined on the basis of ^{1}H and ^{13}C NMR spectra, which exhibited the expected singlet resonances for C_2 symmetry. On the basis of X-ray diffraction studies the two chlorine atoms were assigned to be in a *trans*-orientation in complex **2f** [18]. The same orientation has also been observed in an anisyl derivative of **2** (Ar=4-MeOC$_6$H$_4$) [9]. However, in the case of the related complex $[RuCl_2(PPh_3)(Me_4BPy)]$ (Me_4BPy: 2,6-bis(3,5-dimethylprazol-1-yl)pyridine), a *cis*-configuration was assigned by an X-ray crystallographic study [13]. In another example, reaction of *trans*-$[RuCl_2(C_2H_4)\{N,N,N\text{-}(R,R)\text{-}Ph\text{-}Pybox\}]$ with PPh_3 yields either the *cis*- or *trans*-isomer depending on whether it is refluxed in MeOH or CH_2Cl_2 [12].

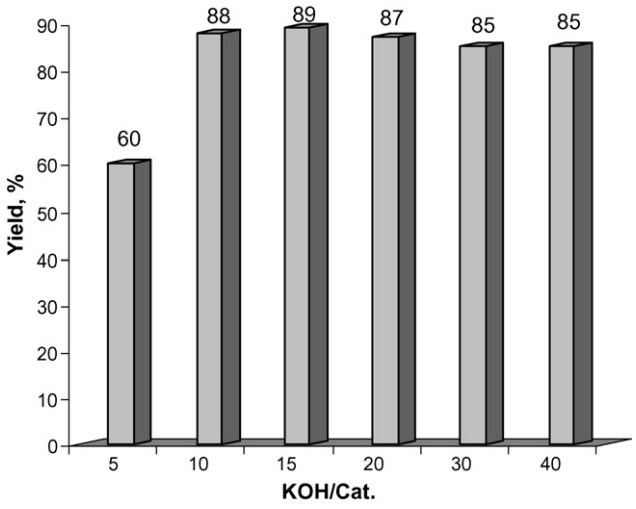


Fig. 1. Optimization of reaction conditions for transfer hydrogenation of acetophenone catalyzed by **3e**.

3.3. Catalytic studies

Studies of the transfer hydrogenation of acetophenone with 2-propanol catalyzed by the complexes were carried out under identical conditions to allow comparison of results.

Preliminary studies were performed using complexes of type **3** as a catalyst as these complexes were structurally similar to ruthenium complexes containing bis(oxazolines) and bis(pyrazolines) ligands [12,13]. Initial experiments using **3d** with ketone:Ru:base in the ratio 1000:1:50 showed limited reactivity (40% yield after 1h). On the basis of these results, we attempted the optimization of the reaction conditions using **4e** as a catalyst (Fig. 1). Reactions were carried out at 82 °C using 10 mmol acetophenone with 0.01 mmol **4e** in 20 mL of 2-propanol for 1 h. As a general feature, a strong dependence was observed on the KOH/catalyst molar ratio, which should not be lower than approximately 10:1. Otherwise, the reaction becomes slower.

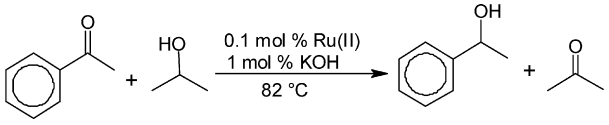
No attempts were made to optimize the catalyst loading, although this could have a favorable bearing on the reactivity; instead identical reaction conditions were used throughout the present study.

To investigate the effect of ancillary ligands, the catalytic activity of MeCN, Pyrazine, and 4,4ï-bipyridine coordinated complexes **2**, **4** and **5** were also studied under the same conditions. As a result, the Pydim-Ru(II) complexes of type **2–5** were found to be active catalysts in the transfer hydrogenation of acetophenone, leading to the formation of *sec*-alcohol with good to excellent conversions (43–99%) in 1 h. The results are summarized in Table 1.

The most remarkable features are:

1. Very rapid conversions are achieved at 82 °C. The reactions become notably slower as the temperature decreases.
2. Under the same reaction conditions, binuclear Ru(II)-arene complexes **6** and **7** furnished less than 7% yield of product.

Table 1
Catalytic activity for transfer hydrogenation of acetophenone catalyzed by Ru(II) complexes



Entries	Catalyst	Conversion (%)
1	**2a**	70
2	**2b**	99 (93)[b](32)[c]
3	**2d**	54
4	**2e**	62
5	**2f**	61
6	**2g**	91
7	**3a**	68
8	**3b**	95
9	**3d**	43
10	**4a**	79
11	**4b**	96
12	**4c**	91
13	**4d**	62
14	**4e**	88
15	**4f**	89
16	**5a**	63
17	**5d**	58
18	**5e**	80
19	**5f**	84
20	**6**	4
21	**7**	7

Reactions were carried out at 82 °C using 10 mmol acetophenone with 0.1 mol% Ru(II) in 20 mL of 2-propanol for 1 h.

[b] Reactions were carried out at 82 °C using 10 mmol acetophenone solution with 0.1 mol% Ru(II) in 20 mL of 2-propanol for 5 min.

[c] Reactions were carried out at 25 °C using 10 mmol acetophenone solution with 0.1mol% Ru(II) in 20 mL of 2-propanol for 1 h.

3. The efficiency of the catalyst seems to depend not only on the imine fragment of the pydim ligands, but also on the ancillary ligands.
4. Mononuclear complexes of type **2** are more active than type **3** complexes. Similarly, the binuclear complexes of type **4** are more active than type **5** complexes.
5. Although all of the Pydim-Ru(II) complexes are active catalysts, **2b**, **3b** and **4b** are much more efficient. Fluorine substituent on the imine fragment of the pydim ligand has been shown to be crucial in the catalytic activity.
6. Catalytic activity decreases when methyl groups are introduced at the *ortho* positions of the aryl ring.

4. Conclusions

This work reports the preparation and characterization of Pydim ligands, mono- and binuclear Pydim-Ru(II) complexes and their catalytic activities for the hydrogen transfer reaction of acetophenone. Useful information has been collected about the influence of several structural factors, including the steric bulkiness around the Ru(II) center and the presence of electron-withdrawing groups on the aromatic ring of the imine fragment of the pydim ligands: (i) if one or two methyl groups were introduced into the *ortho* position of the imine fragment, a constant

decrease in the catalytic yield was observed, which was probably due to a steric effect. ii) When an electron withdrawing group was introduced into the *para* position of the imine fragment, catalytic yield increased. However, if an electron donating group was introduced into the *para* position of the imine fragment, catalytic yield was decreased.

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