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Transfer hydrogenation of aryl ketones with homogeneous ruthenium catalysts containing diazafluorene ligands

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Novel cationic ruthenium(II) complexes bearing a 4,5-diazafluorene unit and *p*-cymene as ligands have been synthesised. The complexes were characterised based on elemental analysis and Fourier transform infrared and nuclear magnetic resonance spectroscopies. The synthesised Ru(II) complexes were employed as pre-catalysts for the transfer hydrogenation of aromatic ketones using 2-propanol as both hydrogen source and solvent in the presence of NaOH. All complexes showed high catalytic activity as catalysts in the reduction of substituted acetophenones to corresponding secondary alcohols. The products of catalysis were obtained with conversion rates of between 80 and 99%. Among the seven new complexes investigated, the most efficient catalyst showed turnover frequencies in the range 255–291 h^{-1} corresponding to 85 to 97% conversion, respectively.

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Keywords: 4,5-diazafluorene; catalysis; transfer hydrogenation; ruthenium; acetophenone

Introduction

After many decades of intensive investigations the synthesis and study of the coordination chemistry of the α-diimine ligands 1,10-phenanthroline and 2,2′-bipyridine have received renewed attention due to their unique electronic properties and catalytic performances.[1–3] Ruthenium(II) complexes bearing 2,2′-bipyridine ligands have unique photochemical and photophysical properties and are mainly used in dye-sensitised solar cells.[4–6] The applications of these ligands in transition metal-mediated catalyses have also been the subject of considerable investigation.[7–12]

Although some aspects of the chemistry of 4,5-diazafluoren-9-one and 4,5-diazafluorene have been studied, little is known regarding the coordination chemistry of these ligands, which are closely related to phenanthroline and bipyridines.[13–19] Recently, a review on the coordination chemistry and applications of metal complexes of various 4,5-diazafluorenes in catalysis, photochemistry and photophysics as well as in bioinorganic chemistry was reported.[20] In recent years, transition metal complexes bearing diazafluorene ligands have attracted considerable interest due to their potential applications in organic devices.[21–28] Nevertheless, the applications of such complexes in catalytic reactions are limited.[29–33]

Compared with other hydrogenation techniques such as using molecular hydrogen, catalytic transfer hydrogenation reactions are characterised by an environmentally benign synthetic process and contribute to industrial applications.[34,35] Catalytic reduction of unsaturated compounds via transfer hydrogenation is one of the most reliable methods of obtaining the corresponding saturated products which are versatile synthetic precursors that yield further functionalised molecules. As catalysts for the transfer hydrogenation of ketones, Ru(II) complexes bearing N, O or P donor ligands have all been used and are known to be effective catalysts.[34,36] Transition metal complexes containing nitrogenous ligands phenanthroline and bipyridine are known to catalyse the reduction of ketones and imines using 2-propanol as hydrogen source in basic medium.[37] Among the various metal complexes, rhodium- and ruthenium-based ones are generally the catalysts of choice for these reactions because they are highly active and selective.[38–40]

We herein report the synthesis of seven new Ru(II) complexes of previously reported bidentate nitrogen ligands derived from 1,10-phenanthroline and their catalytic activities in the transfer hydrogenation of aromatic ketones.

Experimental

Materials and methods

Unless otherwise stated, solvents and materials were used as purchased without further purification. 2-Propanol was dried over CaH_2. The ligands 4,5-diazafluorene-9-one,[41] 1-*H*-cyclopenta [2,1-*b*:3,4-*b*′]-dipyridine-2,5-dione,[42] 1,5-dihydro-2*H*-cyclopenta

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[1,2-*b*:5,4-*b'*]dipyridine-2-one,[43] 4,5-diazaflourene,[44] 9,9'-bis(4,5-diazafluorenyl),[45] 9,9'-bis(4,5-diazafluorenylidene),[46] and *N,N'*-bis (cyclopenta[2,1-*b*:3,4-*b'*]dipyridine-5-ylidine) hydrazine[47] were prepared as described previously. ^{1}H nuclear magnetic resonance (NMR) (400.1 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded using a Bruker Avance 400 spectrometer, with δ referenced to external tetramethylsilane. Fourier transfer infrared (FT-IR) spectra were recorded with a Mattson 1000 ATI UNICAM FT-IR spectrometer as KBr pellets. A Shimadzu LC MS 8040 LC MS/MS triple quadrupole instrument was used for mass spectra analysis due to the inherent characteristics of accurate mass measurements. The elemental analyses for carbon, hydrogen and nitrogen were performed with a Costech Combustion System CHNS-O instrument. Melting points were obtained using a Gallenkamp apparatus with open capillaries and were uncorrected. GC analyses were performed using a Shimadzu GC 2010 Plus equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane; 30 m × 0.32 mm × 0.25 μm). The GC parameters for the transfer hydrogenation of ketones were as follows: initial temperature, 110 °C; initial time, 1 min; solvent delay, 4.48 min; temperature ramp, 80 °C min^{-1}; final temperature, 200 °C; final time, 21.13 min; injector port temperature, 200 °C; detector temperature, 200 °C; injection volume, 2.0 μl.

General procedure for synthesis of ruthenium(II) complexes

[Ru(η$^{[6]}$-*p*-cymene)(μ-Cl)Cl]$_2$ (0.5 equiv. for complexes **1**–**4** or 1 equiv. for complexes **5**–**7**) was added to a solution of ligand (1 equiv.) in CH_2Cl_2 (10 ml) and the mixture was stirred at room temperature for 2 h. The precipitate formed was filtered and washed with dichloromethane and then dried in a vacuum. The residue obtained was dissolved in a minimum amount of water, and a saturated aqueous solution of $[NH_4][PF_6]$ was then added dropwise until no more precipitate formed. The mixture was left to stand for a few hours, after which it was filtered and dried.

Complex ***1***

Yield (89%); m.p. 236–238 °C. FT-IR (KBr, cm^{-1}): 3097, 3045 (aromatic νC H), 2972, 2932, 2878 (aliphatic νC H), 1742 (νC O), 1584 (νC N), 1423 (νC C), 842 (νPF$_6$). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ, ppm): 1.15 (d, 6H, *J* = 6.8 Hz, *p*-cymene $H_{16,17}$), 2.16 (s, 3H, *p*-cymene H_{10}), 2.81 (m, 1H, *p*-cymene H_{15}), 6.11 (d, 2H, *J* = 6.2 Hz, *p*-cymene $H_{13,13'}$), 6.33 (d, 2H, *J* = 6.3 Hz, *p*-cymene $H_{12,12'}$), 7.90 (dd, 2H, *J* = 7.4 and 5.5 Hz, Daf-$H_{2,7}$), 8.39 (d, 2H, *J* = 7.4, Daf-$H_{1,8}$), 9.37 (d, 2H, *J* = 5.5 Hz, Daf-$H_{3,6}$). ^{13}C NMR (100 MHz, DMSO-*d*$_6$, δ, ppm): 185.46 (C_9), 164.96 ($C_{4a/4b}$), 156.73 ($C_{3,6}$), 135.34 ($C_{1,8}$), 130.27 ($C_{2,7}$), 125.72 ($C_{9a/8a}$), 104.55 (C_{11}), 100.75 (C_{14}), 83.04 ($C_{12,12'}$), 82.03 ($C_{13,13'}$), 31.07 (C_{15}), 22.28 ($C_{16,17}$), 18.61 (C_{10}). ESI-MS *m/z*: 453. Anal. Calcd for $C_{21}H_{20}N_2ORuClPF_6$ (%): C, 42.18; H, 3.38; N, 4.69. Found (%): C, 41.82; H, 3.29; N, 4.56.

Complex ***2***

Yield (79%); m.p. 245–247°°C. FT-IR (KBr, cm^{-1}): 3556 (νO H), 3050, 3033 (aromatic νC H), 2961, 2922 (aliphatic νC H), 1689 (νC O), 1610 1576, 1447 (νC N and νC C), 1386 (νC N), 847 (νPF$_6$). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ, ppm): 1.10 (d, 6H, *J* = 6.9 Hz, *p*-cymene $H_{16,17}$), 2.14 (s, 3H, *p*-cymene H_{10}), 2.74 (m, 1H, *p*-cymene H_{15}), 5.90 (d, 2H, *J* = 4.9 Hz, *p*-cymene $H_{13,13'}$), 6.00 (d, 1H, *J* = 4.9 Hz, Daf-H_2), 6.23 (d, 2H, *J* = 4.8 Hz, *p*-cymene $H_{12,12'}$), 7.37 (dd, 1H, *J* = 7.8 and 4.8 Hz, Daf-H_7), 7.55 (d, 1H, *J* = 5.8 Hz, Daf-H_1), 7.92 (d, 1H, *J* = 7.8 Hz, Daf-H_8), 8.99 (d, 1H, *J* = 4.8 Hz, Daf-H_6). ^{13}C NMR (100 MHz, DMSO-*d*$_6$, δ, ppm): 185.30 (C_9), 171.08 (C_3), 170.19 (C_{4a}), 168.93 (C_{4b}), 153.45 (C_6), 132.17 (C_8), 131.59 (C_{8a}), 130.75 (C_7), 128.06 (C_1), 118,86 (C_2), 112.29 (C_{9a}), 103.26 (C_{11}), 99.44 (C_{14}), 82.57, 82.30 ($C_{12,12'}$), 81.57, 80.17 ($C_{13,13'}$), 31.14 (C_{15}), 22.58, 22.09 ($C_{16,17}$), 18.89 (C_{10}). ESI-MS *m/z*: 469. Anal. Calcd for $C_{21}H_{20}N_2O_2RuClPF_6$ (%): C, 41.09; H, 3.29; N, 4.56. Found (%): C, 40.96; H, 3.19; N, 4.48.

Complex ***3***

Yield (85%); m.p. 291–294 °C. FT-IR (KBr, cm^{-1}): 3524 (νO H), 3093 (aromatic νC H), 2967, 2875 (aliphatic νC H), 1628, 1603, 1472, 1414 (νC N, νC C), 1375 (νC N) 837 (νPF$_6$). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ, ppm): 1.08 (d, 6H, *J* = 6.8 Hz, *p*-cymene $H_{16,17}$), 2.17 (s, 3H, *p*-cymene H_{10}), 2.75 (m, 1H, *p*-cymene H_{15}), 4.17 (s, 2H, Daf-H_9), 5.82 (d, 2H, *J* = 6.12 Hz, *p*-cymene $H_{13,13'}$), 6.24 (d, 2H, *J* = 5.9 Hz, *p*-cymene $H_{12,12'}$), 6.92 (d, 1H, *J* = 8.3 Hz, Daf-H_2), 7.65 (dd, 1H, *J* = 7.6 and 5.4 Hz, Daf-H_7), 8.0 (d, 1H, *J* = 8.3 Hz, Daf-H_1), 8.21 (d, 1H, *J* = 7.6 Hz, Daf-H_8), 9.11 (d, 1H, *J* = 5.4 Hz, Daf-H_6). ^{13}C NMR (100 MHz, DMSO-*d*$_6$, δ, ppm): 166.54 (C_3), 162.33 (C_{4a}), 159.05 (C_{4b}), 151,34 (C_6), 139.20 (C_1), 137.19 (C_8), 136.71 (C_{8a}), 128.09 (C_{9a}), 126.12 (C_7), 112.98 (C_2), 104.04 (C_{11}), 100.44 (C_{14}), 83.29, 82.49 ($C_{12,12'}$), 81.44, 80.94 ($C_{13,13'}$), 36.70 (C_9), 31.18 (C_{15}), 22.08 ($C_{16,17}$), 18.89 (C_{10}). ESI-MS *m/z*: 455. Anal. Calcd for $C_{21}H_{20}N_2ORuClPF_6$ (%): C, 42.18; H, 3.38; N, 4.69. Found (%): C, 41.82; H, 3.29; N, 4.56.

Complex ***4***

Yield (90%); m.p. 224–226 °C. FT-IR (KBr, cm^{-1}): 3094 (aromatic νC H), 2969, 2876 (aliphatic νC H), 1597 (νC N), 1421 (νC C), 839 (νPF$_6$). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ, ppm): 1.08 (d, 6H, *J* = 6.8 Hz, *p*-cymene $H_{16,17}$), 2.15 (s, 3H, *p*-cymene H_{10}), 2.75 (m, 1H, *p*-cymene H_{15}), 4.44 (s, 2H, Daf-H_9), 6.07 (d, 2H, *J* = 6.1 Hz, *p*-cymene $H_{13,13'}$), 6.29 (d, 2H, *J* = 5.6 Hz, *p*-cymene $H_{12,12'}$), 7.79 (dd, 2H, *J* = 7.6 and 5.4, Daf-$H_{2,7}$), 8.33 (d, 2H, *J* = 7.6 Hz, Daf-$H_{1,8}$), 9.24 (d, 2H, *J* = 5.4 Hz, $H_{3,6}$). ^{13}C NMR (100 MHz, DMSO-*d*$_6$, δ, ppm): 161.16 ($C_{4a/4b}$), 151.80 ($C_{3,6}$), 137.29 ($C_{2,7}$), 137.15 ($C_{9a/8a}$), 127.10 ($C_{1,8}$), 104.02 (C_{11}), 100.38 (C_{14}), 83.24 ($C_{12,12'}$), 81.72 ($C_{13,13'}$), 37.80 (C_9), 31.07 (C_{15}), 22.18 ($C_{16,17}$), 18,62 (C_{10}). ESI-MS *m/z*: 439. Anal. Calcd for $C_{21}H_{22}N_2RuClPF_6$ (%): C, 43.20; H, 3.81; N, 4.80. Found (%): C, 43.03; H, 3.64; N, 4.62.

Complex ***5***

Yield (93%); m.p. > 300 °C. FT-IR (KBr, cm^{-1}): 3021 (aromatic νC H), 2965, 2871 (aliphatic νC H), 1596 (νC N), 1419 (νC C), 840 (νPF$_6$). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ, ppm): 1.06 (d, 12H, *J* = 6.6 Hz, *p*-cymene $H_{16,17}$), 2.12 (s, 6H, *p*-cymene CH_3Ph, H_{10}), 2.72 (m, 2H, *p*-cymene H_{15}), 5.78 (s, 2H, Daf-H_9), 6.04 (d, 4H, *J* = 4.8 Hz, *p*-cymene $H_{13,13'}$), 6.22 (d, 4H, *J* = 4.8 Hz, *p*-cymene $H_{12,12'}$), 7.56 (b, 4H, Daf-$H_{2,7}$), 7.68 (b, 4H, Daf-$H_{1,8}$), 9.21 (b, 4H, Daf-$H_{3,6}$). ^{13}C NMR (100 MHz, DMSO-*d*$_6$, δ, ppm): 160.43 ($C_{4a/4b}$), 152.94 ($C_{3,6}$), 137.06 ($C_{8a/9a}$), 136.79 ($C_{1,8}$), 127.74 ($C_{2,7}$), 104.30 (C_{11}), 100.19 (C_{14}), 82.88, 82.52 ($C_{12,12'}$), 82.34, 81.88 ($C_{13,13'}$), 49.92 (C_9), 31.04 (C_{15}), 22.29 ($C_{16,17}$), 18.70 (C_{10}). ESI-MS *m/z*: 437. Anal. Calcd for $C_{42}H_{42}N_4Ru_2Cl_2P_2F_{12}$ (%): C, 43.27; H, 3.64; N, 4.81. Found (%): C, 43.31; H, 3.58; N, 4.74.

Complex ***6***

Yield (86%), m.p. > 300 °C. FT-IR (KBr, cm^{-1}): 3094 (aromatic νC H), 2969, 2879 (aliphatic νC H), 1603 (νC N), 1537, 1508 (νC C), 841 (νPF$_6$).[1]HNMR (400 MHz, DMSO-*d*$_6$, δ, ppm): 1.60 (d, 12H, *J* = 5.4 Hz, *p*-cymene $H_{16,17}$), 2.20 (s, 6H, *p*-cymene H_{10}), 2.76–2.86 (m, 2H, *p*-cymene H_{15}), 6.13 (d, 4H, *J* = 5.7 Hz, *p*-cymene $H_{13,13'}$), 6.36 (d, 4H, *J* = 6.0 Hz, *p*-cymene $H_{12,12'}$), 7.88 (dd, 4H, *J* = 7.9 and

5.6 Hz, Daf-$H_{2,7}$), 8.82 (dd, 4H, J = 7.9 and 1.4 Hz, Daf-$H_{1,8}$), 9.35 (dd, 4H, J = 5.6 and 1.4 Hz, Daf-$H_{3,6}$). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 160.70 ($C_{4a/4b}$), 155.37 (C_3), 138.11 (C_9), 132.14 ($C_{1,8}$), 129.63 ($C_{8a/9a}$), 126.57 ($C_{2,7}$), 104.55 (C_{11}), 100.93 (C_{14}), 83.46 ($C_{12,12'}$), 81.99 ($C_{13,13'}$), 31.13 (C_{15}), 22.25 ($C_{16,17}$), 18.66 (C_{10}). ESI-MS m/z: 437. Anal. Calcd for $C_{42}H_{40}N_4Ru_2Cl_2P_2F_{12}$ (%): C, 43.35; H, 3.47; N, 4.82. Found (%): C, 43.24; H, 3.40; N, 4.64.

Complex ***7***

Yield (76%); m.p. > 300 °C. FT-IR (KBr, cm^{-1}): 3092 (aromatic νC H), 2967, 2875 (aliphatic νC H), 1599 (νC N), 1543, 1416 (νC C), 839 (νPF_6). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.16 (d, 12H, J = 6.6 Hz, *p*-cymene $H_{16,17}$), 2.18 (s, 6H, *p*-cymene H_{10}), 2.77–2.86 (m, 2H, *p*-cymene H_{15}), 6.12 (d, 4H, J = 5.7 Hz, *p*-cymene $H_{13,13'}$), 6.35 (d, 4H, J = 6.3 Hz, *p*-cymene $H_{12,12'}$), 7.83 (dd, 2H, J = 7.7 and 4.4 Hz, Daf-H_7), 7.99 (dd, 2H, J = 7.7 and 4.6 Hz, Daf-H_2), 8.71–8.83 (m, 4H, Daf-$H_{1,8}$), 9.34 (d, 2H, J = 4.4 Hz, Daf-H_6), 9.40 (d, 2H, J = 4.6 Hz, H_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 162.15 and 161.96 (C_3 and C_6), 157.68 (C_9), 155.28 ($C_{4a/4b}$), 140.52 (C_1), 135.22 (C_8), 130.20 (C_2), 128.94 (C_7), 125.78 ($C_{8a/9a}$), 104.61 (C_{11}), 100.60 (C_{14}), 83.14 ($C_{12,12'}$), 81.90 ($C_{13,13'}$), 31.10 (C_{15}), 22.26 ($C_{16,17}$), 18.62 (C_{10}). ESI-MS m/z: 450.70. Anal. Calcd for $C_{42}H_{40}N_6Ru_2Cl_2P_2F_{12}$ (%): C, 42.33; H, 3.39; N, 7.05. Found (%): C, 42.20; H, 3.28; N, 7.01.

General procedure for transfer hydrogenation of ketones

A solution of complex, NaOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed isopropanol (5 ml) were refluxed. Subsequently a sample of the reaction mixture was taken off, diluted with acetone and analysed immediately using GC. Conversions obtained are related to the residual unreacted ketone.

Results and discussion

Ligands were prepared as described previously. Ruthenium(II) complexes were prepared by the reaction of corresponding ligands (1 equiv.) with [Ru(η[6]-*p*-cymene)(μ-Cl)Cl]$_2$ (0.5 equiv. for complexes **1**–**4** or 1 equiv. for complexes **5**–**7**) in CH_2Cl_2. The ruthenium complexes were isolated as analytically pure hexafluorophosphate salts (Figs 1–7).

The ^{1}H NMR spectra of complexes **1**–**7** showed characteristic features of both 4,5-diazafluorene moiety and *p*-cymene ligand. In the ^{1}H NMR spectra of complexes **1**, **4**, **5**, **6** and **7**, protons of the unsubstituted ring of 4,5-diazafluorene formed a characteristic pattern comprising three sets of peaks. Compared to free ligands, these protons were shifted to lower field upon complexation with Ru(II). Protons of the substituted ring of 4,5-diazafluorene moiety in complexes **2** and **3** appeared as two doublets. 1*H*-cyclopenta [2,1-*b*:3,4-*b*′]-dipyridine-2,5-dione and 1,5-dihydro-2*H*-cyclopenta [1,2-*b*:5,4-*b*′]dipyridine-2-one have two C O groups in position 2 which can be isomerised to their enolic forms with the involvement of the NH group in solution.[38,39] Similar keto–enol tautomerism

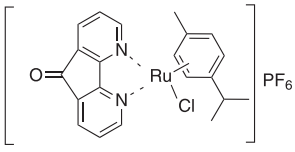


Figure 1. Structure of complex **1**.

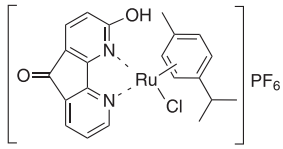


Figure 2. Structure of complex **2**.

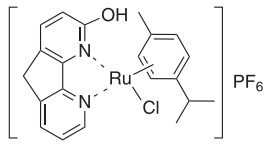


Figure 3. Structure of complex **3**.

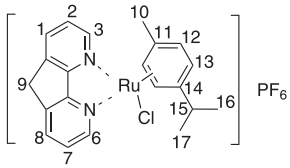


Figure 4. Structure of complex **4**.

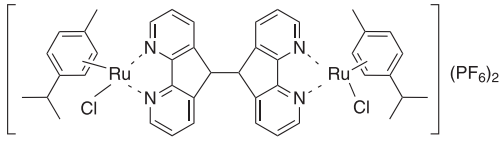


Figure 5. Structure of complex **5**.

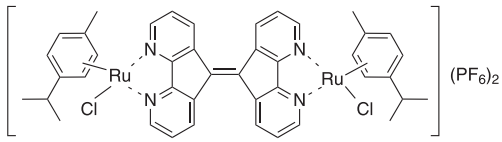


Figure 6. Structure of complex **6**.

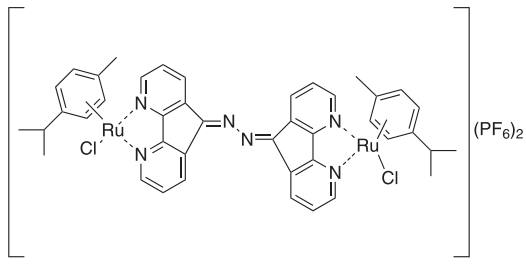


Figure 7. Structure of complex **7**.

was also reported in the case of 6,6′-dihydroxy-2,2′-bipyridyl ligand.[48] The signals consisting of two doublets between 5.92–6.13 and 6.15–6.33 ppm were assigned to the presence of aromatic protons in the *p*-cymene group. The spectra of the complexes also exhibited signals at around 2.76 and 1.10 ppm

due to the CH and CH_3 of the isopropyl group of the *p*-cymene moiety, respectively. Finally, the resonance of methyl protons in the *p*-cymene groups was observed at about 2.15 ppm. The $^{13}C–\{^1H\}$ NMR spectra of complexes **1**–**7** display all the signals typical for both diazafluorene moiety and arene ligand *p*-cymene.

Compared with the FT-IR spectra of the ligands, the sharp absorptions at 1655 and 1651 cm^{-1} due to pyridinone C O groups in the ligands disappeared in the spectra of the corresponding complexes **2** and **3**, respectively. The broad absorptions at 3556 and 3524 cm^{-1} were assigned to ν(O H) in complexes **2** and **3**, respectively. The disappearance of the pyridinone carbonyl group bands and the appearance of new broad signals above 3520 cm^{-1} in the FT-IR spectra of these two complexes were indicative of isomerisation of the C O groups to their enol forms with the involvement of NH groups (Fig. 8). Furthermore, the presence of the PF_6 group in all complexes is also evident from the IR absorption bands between 837 and 847 cm^{-1}. Satisfactory elemental analyses were obtained for all complexes.

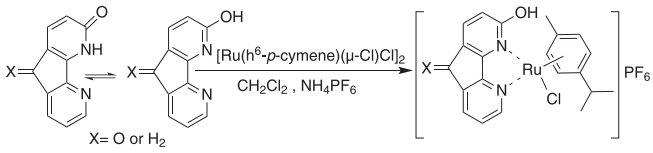
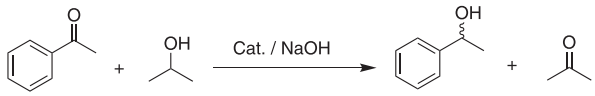


Figure 8. Keto–enol forms of 1*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dipyridine-2,5-dione and 1,5-dihydro-2*H*-cyclopenta[1,2-*b*:5,4- *b*′]dipyridine-2-one and their corresponding complexes **2** and **3**.

To evaluate the effectiveness of Ru(II) complexes **1**–**7** as pre-catalysts in transfer hydrogenation reactions of aromatic ketones, we preferred starting with the reduction of acetophenone as the model substrate. For screening reaction activity, the optimal conditions were investigated, such as reaction temperature and molar ratio of substrate to catalyst. The catalytic results collected from the test reactions are summarised in Table 1. As can be inferred from the table, at room temperature no appreciable formation of 1-phenylethanol was observed and pre-catalyst and the presence of NaOH are required to obtain appreciable conversion. The catalytic activity of $[Ru(\eta_6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ under the applied experimental conditions is negligible. As evident from Table 1, the reaction rate was significantly increased when the temperature increased to 82 °C. The reactivity decreased sharply with increasing substrate concentration, by tenfold.

Based on our investigation of the optimal conditions, we also evaluated the transfer hydrogenation of substituted aromatic ketones using 2-propanol as both hydrogen source and solvent in the presence of complexes **1**–**7** as catalysts. The results presented in Table 2 showed that all substituted acetophenones were reduced to corresponding secondary alcohols in high yields. The results clearly indicated that the electronic properties of the

Table 1. Transfer hydrogenation of acetophenone catalysed by **1**–**7**



Entry	Complex	S/C/base[a]	Reaction time (h)		Conversion (%)[b]		TOF (h^{-1})[c]	
			25 °C	82 °C	25 °C	82 °C	25 °C	82 °C
1	**1**	100:1:5	24	0.5	12	95	<1	190
2	**1**	100:1		24		—		—
3	**1**	1000:1:5		1		14		14
4	**2**	100:1:5	24	0.5	13	96	<1	192
5	**2**	100:1		24		—		—
6	**2**	1000:1:5		1		11		11
7	**3**	100:1:5	24	0.33	13	97	<1	291
8	**3**	100:1		24		—		—
9	**3**	1000:1:5		1		16		16
10	**4**	100:1:5	24	0.75	10	96	<1	128
11	**4**	100:1		24		—		—
12	**4**	1000:1:5		2		8		6
13	**5**	100:1:5	24	0.75	48	97	2	129
14	**5**	100:1		24		—		—
15	**5**	1000:1:5		1		18		18
16	**6**	100:1:5	24	1	25	82	1	82
17	**6**	100:1		24		—		—
18	**6**	1000:1:5		2		18		9
19	**7**	100:1:5	24	2	30	98	1	49
20	**7**	100:1		24		—		—
21	**7**	1000:1:5		2		16		8

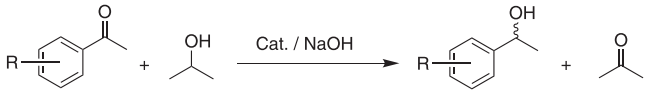
Reaction conditions: all reactions carried out in 2-propanol.

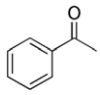
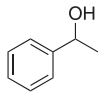
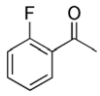
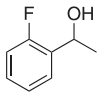
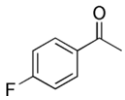
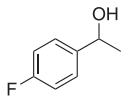
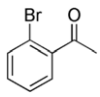
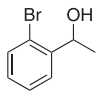
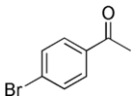
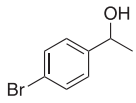
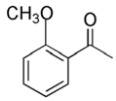
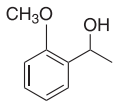
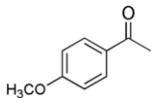
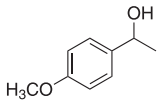
[a]S/C/base: acetophenone/complex/NaOH

[b]Determined by GC (three independent catalytic experiments).

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

Table 2. Transfer hydrogenation of substituted acetophenones catalysed by **1–7**[a]



Entry	Catalyst	Substrate	Product	Time (min)	Conv. (%)[b]	TOF (h^{-1})[c]
1	**1**			30	95	190
2	**2**			30	96	192
3	**3**			20	97	291
4	**4**			45	96	128
5	**5**			45	97	129
6	**6**			60	82	82
7	**7**			120	98	49
8	**1**			30	97	194
9	**2**			30	96	192
10	**3**			20	95	285
11	**4**			45	96	128
12	**5**			45	95	127
13	**6**			60	87	87
14	**7**			120	98	49
15	**1**			30	98	196
16	**2**			30	99	198
17	**3**			20	97	291
18	**4**			45	99	132
19	**5**			45	98	131
20	**6**			60	92	92
21	**7**			120	99	50
22	**1**			30	94	188
23	**2**			30	93	186
24	**3**			20	92	276
25	**4**			45	93	124
26	**5**			45	93	124
27	**6**			60	81	81
28	**7**			120	85	48
29	**1**			30	96	192
30	**2**			30	95	190
31	**3**			20	95	285
32	**4**			45	96	128
33	**5**			45	96	128
34	**6**			60	84	84
35	**7**			120	98	49
36	**1**			30	92	184
37	**2**			30	90	180
38	**3**			20	88	264
39	**4**			45	87	116
40	**5**			45	85	113
41	**6**			60	80	80
42	**7**			120	92	46
43	**1**			30	89	178
44	**2**			30	88	176
45	**3**			20	85	255
46	**4**			45	82	109
47	**5**			45	80	107
48	**6**			60	76	76
49	**7**			120	90	45

[a]Catalyst (0.005 mmol), substrate (0.5 mmol), NaOH (0.025 mmol), *i*PrOH (5 ml).
[b]Purity of compounds checked by NMR and GC. Yields are based on methyl aryl ketone.
[c]TOF = (mol product/mol catalyst) × h^{-1}.

substituent on the aromatic ring changed the reduction rate. The introduction of an electron-withdrawing group on the phenyl ring of the ketone decreased the electron density of the C O bond so that the activity was improved.[49,50] Table 2 also shows that 2-substituted acetophenones were reduced more slowly than 4-substituted acetophenones, probably because of an undesirable steric clash. However, using complexes **1**–**7** as catalysts under identical conditions, the hydrogenation of 2-methoxyacetophenone occurred more rapidly than that of 4-methoxyacetophenone. The lower reactivity of 4-methoxyacetophenone towards the hydrogenation reaction may be attributed to its low redox potential.[51]

The catalytic evaluation for the studied hydrogen transfer reactions revealed that complex **3** was the most efficient catalyst among the seven new complexes described herein. The turnover frequencies (TOFs) obtained using this catalyst ranged from 255 to 291 h^{-1}, corresponding to 85 to 97% conversions, respectively.

Conclusions

In summary, we synthesised seven new Ru(II) complexes bearing a 4,5-diazafluorene unit and an arene ligand. The Ru(II) complexes were employed as precursors of catalysts in the hydrogen transfer reaction of aromatic ketones using 2-propanol as the hydrogen source. The results indicated that complex **3** showed the highest activity with TOFs between 255 (85%) and 291 h^{-1} (97%).

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