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Ruthenium(II) carbonyl chloride complexes containing pyridine-functionalised bidentate N-heterocyclic carbenes: Synthesis, structures, and impact of the carbene ligands on catalytic activities

Xiao-Wei Li [a], Gao-Feng Wang [a], Fei Chen [a], Yi-Zhi Li [a], Xue-Tai Chen [a,*], Zi-Ling Xue [b]

[a] State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China
[b] Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

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ABSTRACT

A series of new ruthenium(II) carbonyl chloride complexes with pyridine-functionalised N-heterocyclic carbenes [Ru(Py-NHC)$(CO)_2Cl_2$], [Py-NHC = 3-methyl-1-(2-pyridyl)imidazol-2-ylidene, **1** (**1a** and **1b**); 3-methyl-1-(2-picoyl)imidazol-2-ylidene, **2** (**2a** and **2b**); 3-methyl-1-(2-pyridyl)benzimidazolin-2-ylidene, **3** (**3b**); 3-methyl-1-(2-picoyl)benzimidazolin-2-ylidene, **4** (**4a** and **4b**); 1-methyl-4-(2-pyridyl)-1,2,4-triazoline-5-ylidene, **5** (**5a** and **5b**)] have been prepared by transmetallation from the corresponding silver carbene complexes and characterized by NMR, IR spectroscopy and elemental analysis. In these complexes with bidentate Py-NHC ligands, one CO ligand is *trans* to the Py ligand. In **1a**, **2a**, **4a**, and **5a**, the NHC ligand is *trans* to the other CO ligand, thus leaving the two Cl^- ligands trans to each other. In **1b**, **2b**, **3b**, **4b**, and **5b**, the NHC ligands are *trans* to one Cl^- ligand, and the two Cl^- ligands are cis to each other. The structures for **1b**, **2b**, **3b** and **4b** have been determined by single-crystal X-ray diffraction. These complexes are efficient catalysts in the transfer hydrogenation of acetophenone and their catalytic activities are found to be influenced by electronic effect of the N-heterocyclic carbene ligands.

1. Introduction

N-Heterocyclic carbenes (NHCs) have become increasingly important ligands in organometallic chemistry and homogeneous catalysis [1–7] ever since the isolation of free NHCs by Arduengo and co-workers in 1991 [8]. NHCs are known to be strong electron donor ligands to metal centers. Compared to phosphine complexes, NHC complexes have better thermal and air stability [9–11]. N-Heterocyclic carbenes (NHCs) are generally derived from imidazoles [12–16], benzimidazoles [17–20], triazoles [21–24] and pyrazoles [25–29], and they are often functionalised on both nitrogen atoms by introducing the substituents. Catalytic properties of these NHC complexes are usually enhanced by these substituents with tunable steric and electronic effect. Recently, there have been reports of a large number of new metal complexes bearing NHC ligands and the use of these complexes in catalysis reactions such as transfer hydrogenation [30–34], Heck or Suzuki C–C coupling [35–40], and hydrosilylation [31]. Ligands with one NHC and one pyridine group are among those actively investigated [41–44]. Our group has prepared a series of ruthenium carbonyl chloride complexes bearing pyridine-functionalised, bidentate imidazole-based carbene ligands and tested their catalytic activities in the transfer hydrogenation of acetophenone [30]. To our knowledge, ruthenium(II) carbonyl chloride complexes containing pyridine-functionalised, bidentate, benzimidazole and triazole ring-based NHC ligands have not been reported. In this paper, we report the synthesis and characterization of a series of new ruthenium(II) complexes with such carbene ligands, along with the catalytic activities of these complexes in transfer hydrogenation of ketones which reveal the electronic effect of the Py-NHC ligands on the catalytic activities.

2. Experimental

2.1. General procedures

All manipulations were performed under nitrogen using standard Schlenk techniques. $[Ru(CO)_2Cl_2]_n$ [45] and carbene precursor salt **L1** [46,47], **L2** [13], **L3** [48–50], and **L4** [36] were prepared according to the reported literatures. MeOH was dried over Mg. CH_2Cl_2 and CH_3CN were distilled from CaH_2 under nitrogen. Other solvents were used as received as technical grade solvents. All remaining chemicals were purchased from Acros and used as received without further purification. NMR data were recorded on a Bruker AM-500 spectrometer with TMS as internal standard.

* Corresponding author. Fax: +86 25 83314502.
E-mail address: xtchen@netra.nju.edu.cn (X.-T. Chen).

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Elemental analyses (C, H and N) were carried out on a Perkin–Elmer 240C analytic instrument. IR spectra were performed on a Nicolet NEXUS870 FT-IR spectrometer. The catalytic data were collected by GC-9560 equipment.

2.2. Synthesis of compounds

2.2.1. 1-Methyl-4-(2-pyridyl)-1,2,4-triazolium iodide (**L5**)

A solution of 4-(2-pyridyl)-1,2,4-triazole [51] (1.00 g, 6.85 mmol) and iodomethane (1.94 g, 13.69 mmol) in acetone (50 ml) was stirred at 60 °C for 12 h. The reaction mixture was filtered and the precipitate was washed three times with Et_2O and dried in vacuo to obtain a white powder. Yield: 1.68 g (85%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 10.96 (s, 1H, CH_3NCHN), 9.99 (s, 1H, NC*H*N), 8.70 (d, 1H, $^3J_{H-H}$ = 4.5 Hz, 6-*H* of Py), 8.28 (t, 1H, $^3J_{H-H}$ = 6.5 Hz, 5-*H* of Py), 8.06 (d, 1H, ^3J = 8 Hz, 3-*H* of Py), 7.73–7.70 (m, 1H, 4-*H* of Py), 4.18 (s, 3H, C*H*$_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 144.81 (CH_3N*C*HN), 139.99 (N*C*HN), 136.80, 136.54, 136.14, 121.29, 110.45 (Py–*C*), 34.51 (*C*H$_3$). *Anal.* Calc. for $C_8H_9N_4I$: C, 33.32; H, 3.12; N, 19.44. Found: C, 33.25; H, 3.03; N, 19.36%.

2.2.2. {[3-Methyl-1-(2-pyridyl)imidazol-2-ylidene]Ru(CO)$_2$Cl$_2$} **1** (**1a** and **1b**)

A mixture of **L1** (0.20 g, 0.8 mmol) and silver(I) oxide (0.19 g, 0.8 mmol) in 40 ml of CH_2Cl_2 was stirred at room temperature for 24 h under exclusion of light, and then $[Ru(CO)_2Cl]_n$ (0.18 g, 0.8 mmol) was added. The mixture was stirred for 24 h again. The resulting solution was filtered through Celite and the solvent was removed under vacuum, the crude residue was purified by column chromatography. Elution with CH_2Cl_2: acetone (10:1) afforded **1a** as a pale yellow solid, and then elution with CH_2Cl_2: acetone (5:1) yielded **1b** as a yellow solid.

Complex **1a**: Yield: 0.10 g (32%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 9.03 (d, 1H, $^3J_{H-H}$ = 5 Hz, 6-*H* of Py), 8.47 (s, 1H, 4,5-imidazol-2-ylidene *H*), 8.33 (t, 1H, $^3J_{H-H}$ = 1.5 Hz, 5-*H* of Py), 8.25 (d, 1H, $^3J_{H-H}$ = 8 Hz, 3-*H* of Py), 7.72 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.64 (t, 1H, $^3J_{H-H}$ = 6 Hz, 4-*H* of Py), 4.09 (s, 3H, C*H*$_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 203.38, 196.89 (CO), 190.79 (Ru–C), 156.28, 145.88, 132.06, 128.95, 127.35, 120.53, 116.13 (Py–*C* and 4,5-imidazol-2-ylidene *C*), 41.18 (*C*H$_3$). *Anal.* Calc. for $C_{11}H_9N_3O_2Cl_2Ru$: C, 34.12; H, 2.34; N, 10.85. Found: C, 34.02; H, 2.21; N, 10.72%. FT-IR (KBr, cm^{-1}): ν_{CO} 2062 and 1994 cm^{-1}.

Complex **1b**: Yield: 0.09 g (29%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 9.23 (d, 1H, $^3J_{H-H}$ = 5.5 Hz, 6-*H* of Py), 8.47 (s, 1H, 4,5-imidazol-2-ylidene *H*), 8.35 (t, 1H, $^3J_{H-H}$ = 8.5 Hz, 5-*H* of Py), 8.23 (d, 1H, $^3J_{H-H}$ = 8.5 Hz, 3-*H* of Py), 7.93 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.69 (t, 1H, $^3J_{H-H}$ = 6.5 Hz, 4-*H* of Py), 3.93 (s, 3H, C*H*$_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 202.88, 195.26(*C*O), 183.71 (Ru–*C*), 156.95, 153.62, 147.83, 131.20, 128.01, 122.74, 117.80 (Py–*C* and 4,5-imidazol-2-ylidene *C*), 35.91 (*C*H$_3$). *Anal.* Calc. for $C_{11}H_9N_3O_2Cl_2Ru$: C, 34.12; H, 2.34; N, 10.85. Found: C, 33.98; H, 2.19; N, 10.68%. FT-IR (KBr, cm^{-1}): ν_{CO} 2060 and 1996 cm^{-1}.

2.2.3. {[3-Methyl-1-(2-picoyl)imidazol-2-ylidene]Ru(CO)$_2$Cl$_2$} **2** (**2a** and **2b**)

The complexes were prepared, following a procedure similar to that for **1a** and **1b**, using the carbene precursor salt **L2** (0.20 g, 0.79 mmol), silver(I) oxide (0.18 g, 0.79 mmol) and $[Ru(CO)_2Cl]_n$ (0.18 g, 0.79 mmol). Initial elution with CH_2Cl_2: acetone (30:1) gave **2a** as a pale yellow solid. Subsequently elution with CH_2Cl_2:acetone (10:1) produced **2b** as a yellow solid.

Complex **2a**: Yield: 0.13 g (40%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 9.08 (d, 1H, $^3J_{H-H}$ = 5.5 Hz, 6-*H* of Py), 8.14 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, 5-*H* of Py), 7.77 (d, 1H, $^3J_{H-H}$ = 7.5 Hz, 3-*H* of Py), 7.65 (t, 1H, $^3J_{H-H}$ = 7 Hz, 4-*H* of Py), 7.58 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.48 (s, 1H, 4,5-imidazol-2-ylidene *H*), 5.84 (s, 2H, C*H*$_2$ linker), 4.02 (s, 3H, C*H*$_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 200.05, 192.94 (*C*O), 175.18 (Ru–*C*), 157.47, 156.04, 140.95, 126.33, 125.57, 123.90, 122.67 (Py–*C* and Ar–*C*), 53.34(*C*H$_2$), 37.80(*C*H$_3$). *Anal.* Calc. for $C_{12}H_{11}N_3O_2Cl_2Ru$: C, 35.92; H, 2.76; N, 10.47. Found: C, 36.04; H, 2.74; N, 10.24%. FT-IR (KBr, cm^{-1}): ν_{CO} 2044 and 1971 cm^{-1}.

Complex **2b**: Yield: 0.07 g (21%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 9.35 (d, 1H, $^3J_{H-H}$ = 5.5 Hz, 6-*H* of Py), 8.14 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, 5-*H* of Py), 7.76 (d, 1H, $^3J_{H-H}$ = 7.5 Hz, 3-*H* of Py), 7.68 (t, 1H, $^3J_{H-H}$ = 6.5 Hz, 4-*H* of Py), 7.61 (s, 1H, 4,5-imidazol-2-ylidene *H*), 7.47 (s, 1H, 4,5-imidazol-2-ylidene *H*), 5.80 (d, 1H, $^2J_{H-H}$ = 16 Hz, C*HH* linker), 5.23 (d, 1H, $^2J_{H-H}$ = 16.5 Hz, C*HH* linker), 3.95 (s, 3H, C*H*$_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 197.94, 193.39 (*C*O), 177.82 (Ru–*C*), 155.34, 154.14, 140.71, 125.06, 124.55, 123.02, 122.65 (Py–*C* and Ar–*C*), 54.77 (*C*H$_2$), 37.92 (*C*H$_3$). *Anal.* Calc. for $C_{12}H_{11}N_3O_2Cl_2Ru$: C, 35.92; H, 2.76; N, 10.47. Found: C, 36.07; H, 2.81; N, 10.32%. FT-IR (KBr, cm^{-1}): ν_{CO} 2052 and 1979 cm^{-1}.

2.2.4. {[3-Methyl-1-(2-pyridyl)benzimidazolin-2-ylidene]Ru(CO)$_2$Cl$_2$} **3** (**3b**)

A mixture of **L3** (0.20 g, 0.56 mmol), $Ru(CO)_2Cl_2$ (0.13 g, 0.56 mmol) and NEt_3 (0.31 ml, 2.24 mmol) in 40 ml of CH_3CN was stirred at room temperature until a pale yellow precipitate was formed. The resulting solid was filtered and then recrystallised from CH_2Cl_2/MeOH to give yellow crystals. Yield: 0.09 g (35%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 9.42 (d, 1H, $^3J_{H-H}$ = 5.5 Hz, 6-*H* of Py), 8.66 (d, 1H, $^3J_{H-H}$ = 8 Hz, Ar-*H*), 8.52 (d, 1H, $^3J_{H-H}$ = 7 Hz, Ar-*H*), 8.43 (t, 1H, $^3J_{H-H}$ = 8.5 Hz, 5-*H* of Py), 8.00 (d, 1H, $^3J_{H-H}$ = 8.5 Hz, 3-*H* of Py), 7.76 (t, 1H, $^3J_{H-H}$ = 6.5 Hz, 4-*H* of Py). 7.66–7.61 (m, 2H, Ar-*H*), 4.22 (s, 3H, C*H*$_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 197.73, 193.05 (CO), 190.02 (Ru–*C*), 152.82, 149.33, 143.31, 135.89, 130.55, 125.81, 125.73, 122.89, 114.07, 113.26, 112.89 (Py–*C* and Ar–*C*), 35.69 (*C*H$_3$). *Anal.* Calc. for $C_{15}H_{11}N_3O_2Cl_2Ru$: C, 41.20; H, 2.54; N, 9.61. Found: C, 41.19; H, 2.53; N, 9.53%. FT-IR (KBr, cm^{-1}): ν_{CO} 2056 and 1990 cm^{-1}.

2.2.5. {[3-Methyl-1-(2-picoyl)benzimidazolin-2-ylidene]Ru(CO)$_2$Cl$_2$} **4** (**4a** and **4b**)

The complexes were prepared by a procedure analogous to that for **1a** and **1b** using the carbene precursor salt **L4** (0.20 g, 0.77 mmol), silver(I) oxide (0.18 g, 0.77 mmol) and $[Ru(CO)_2Cl]_n$ (0.18 g, 0.77 mmol). Elution with CH_2Cl_2 initially gave **4a** as a pale

Table 1
Selected bond lenghs (Å) and bond angles (°) for complex **1b**, **2b**, **3b** and **4b**.

	1b	2b	3b	4b
Bond lengths				
Ru1–C3	2.014(3)	2.006(5)	2.002(3)	2.029(2)
Ru1–N3	2.152(2)	2.172(4)	2.132(3)	2.1630(18)
Ru1–Cl1	2.4538(8)	2.4822(11)	2.4548(10)	2.4646(6)
Ru1–Cl2	2.4318(8)	2.4262(12)	2.4730(10)	2.4279(7)
Ru1–C10	1.874(3)	1.859(5)	1.891(4)	1.866(3)
Ru1–C11	1.878(3)	1.869(5)	1.884(4)	1.853(3)
Bond angles				
C10–Ru1–C3	98.88(12)	96.8(2)	93.66(15)	93.96(10)
C11–Ru1–C3	92.93(11)	93.3(2)	100.94(15)	93.65(10)
C10–Ru1–N3	174.72(11)	176.54(19)	91.71(14)	176.92(10)
C11–Ru1–N3	93.92(10)	91.86(18)	176.94(14)	94.14(9)
C3–Ru1–N3	77.51(10)	85.86(17)	77.40(12)	84.55(8)
C3–Ru1–Cl2	90.12(7)	87.31(14)	86.49(10)	91.43(6)
N3–Ru1–Cl2	86.69(6)	87.14(11)	88.23(8)	87.67(6)
C3–Ru1–Cl1	170.74(8)	176.22(14)	171.25(9)	173.71(7)
N3–Ru1–Cl1	93.24(6)	91.50(11)	94.08(8)	89.33(5)

yellow solid. Subsequent elution with CH_2Cl_2: acetone (20: 1) yielded **4b** as a yellow solid.

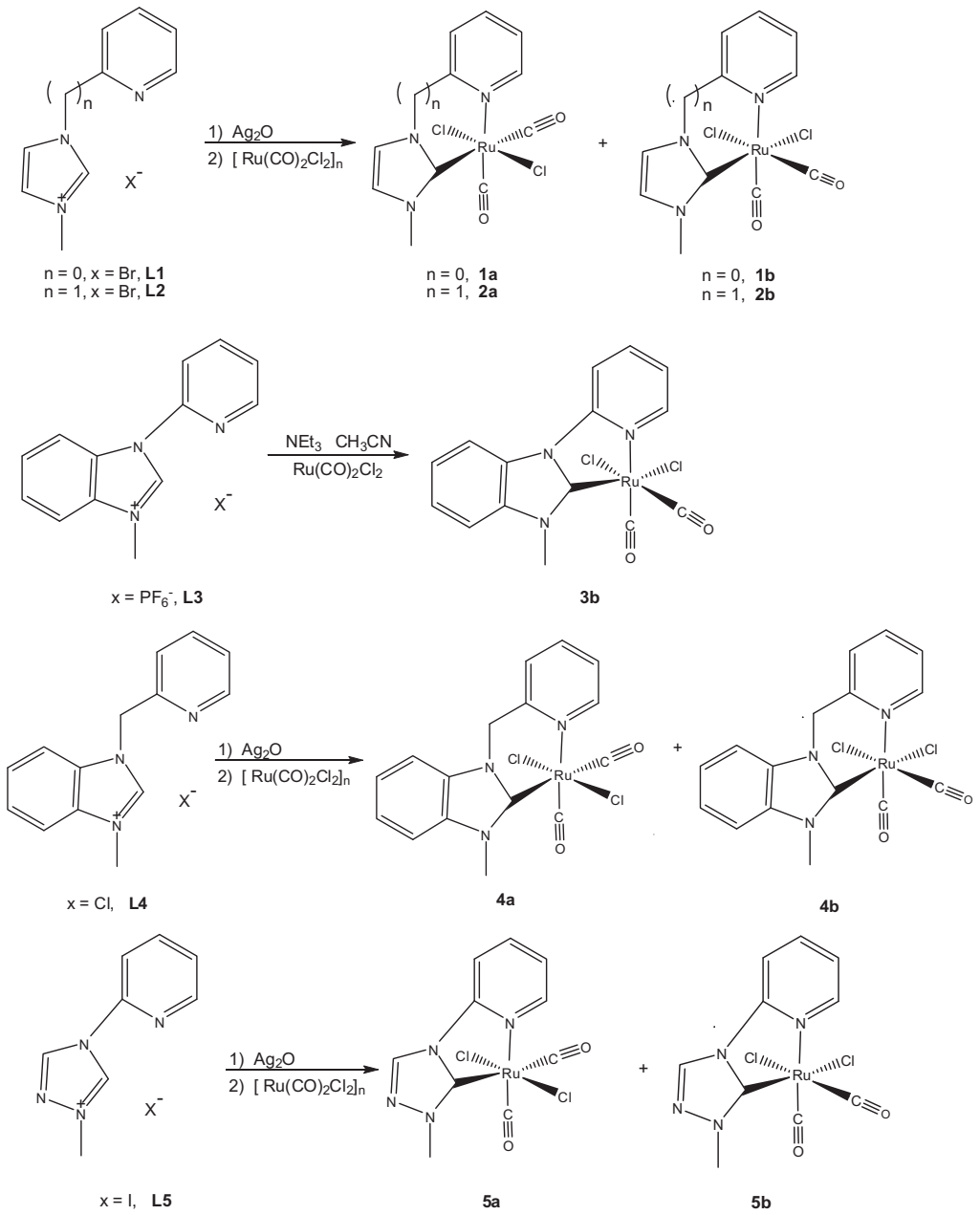
Complex **4a**: Yield: 0.15 g (42%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 9.13 (d, 1H, $^3J_{H-H}$ = 5.5 Hz, 6-*H* of Py), 8.17–7.49 (m, 7H, Ar-*H*, Py-*H*), 6.20 (s, 2H, NCH_2-pyridine), 4.28 (s, 3H, C*H*3). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 200.7, 193.42 (*C*O), 180.65 (Ru–*C*), 156.37, 153.02, 140.22, 134.08, 131.75, 125.31, 123.16, 122.78, 121.98, 111.53, 110.28 (Py–*C* and Ar–*C*), 50.01 (*C*H_2), 34.68 (*C*H_3). *Anal.* Calc. for $C_{16}H_{13}N_3O_2Cl_2Ru$: C, 42.58; H, 2.90; N, 9.31. Found: C, 42.42; H, 2.81; N, 9.31%. FT-IR (KBr, cm^{-1}): ν_{CO} 2050 and 1976 cm^{-1}.

Complex **4b**: Yield: 0.14 g (39%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 9.37 (d, 1H, $^3J_{H-H}$ = 5.5 Hz, 6-*H* of Py), 8.16–7.46 (m, 7H, Ar-*H*, Py-*H*), 6.30 (d, 1H, $^2J_{H-H}$ = 16.5 Hz, C*HH* linker), 5.40 (d, 1H, $^2J_{H-H}$ = 16.5 Hz, C*HH* linker), 4.19 (s, 3H, CH_3). ^{13}C NMR(DMSO-d_6, 125 MHz): δ 197.47, 192.82 (*C*O), 181.84 (Ru–*C*), 155.37, 154.05, 140.83, 135.02, 133.69, 125.17, 125.22, 124.32, 124.15, 111.63, 111.17 (Py–*C* and Ar–*C*), 51.15 (*C*H_2), 34.82 (*C*H_3). *Anal.* Calc. for $C_{16}H_{13}N_3O_2Cl_2Ru$: C, 42.58; H, 2.90; N, 9.31. Found: C, 42.40; H, 2.83; N, 9.27%. FT-IR (KBr, cm^{-1}): ν_{CO} 2057 and 1996 cm^{-1}.

2.2.6. {[1-methyl-4-(2-pyridyl)-1,2,4-triazoline-5-ylidene]Ru(CO)$_2$Cl$_2$} **5** (**5a** and **5b**)

A mixture of **L5** (0.20 g, 0.69 mmol) and silver(I) oxide (0.16 g, 0.69 mmol) in 30 ml of MeOH was stirred at room temperature for 24 h under exclusion of light, and then solvent was removed completely under vacuum. $[Ru(CO)_2Cl]_n$ (0.16 g, 0.69 mmol) in 30 ml of CH_2Cl_2 was added to the solid, and the mixture was stirred overnight and filtered. The crude product was purified by column chromatography first using CH_2Cl_2: acetone (10:1) to give **5a**, and then using CH_2Cl_2: acetone (3:1) to give **5b**.

Complex **5a**: Yield: 0.12 g (45%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 9.95 (s, 1H, NC*H*N), 9.12 (d, 1H, $^3J_{H-H}$ = 5.5 Hz, 6-*H* of Py), 8.47–8.41 (m, 2H, 3,5-*H* of Py), 7.74 (t, 1H, $^3J_{H-H}$ = 6 Hz, 4-*H*



Scheme 1. Synthesis of ruthenium(II) carbonyl complex **1a**, **1b**, **2a**, **2b**, **3b**, **4a**, **4b**, **5a** and **5b**.

of Py), 4.31 (s, 3H, C*H*3). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 199.81, 193.36 (*C*O), 186.99 (Ru–*C*), 153.72, 149.25, 143.29, 140.51, 125.89, 114.67 (N*C*HN and Py–*C*), 39.46 (*C*H$_3$). *Anal.* Calc. for $C_{10}H_8N_4O_2Cl_2Ru$: C, 30.94; H, 2.08; N, 14.43. Found: C, 30.91; H, 2.06; N, 14.43%. FT-IR (KBr, cm^{-1}): ν_{CO} 2067 and 2007 cm^{-1}.

Complex **5b**: Yield: 0.02 g (7%). ^{1}H NMR (500 MHz, DMSO-d_6, 298 K): δ 9.97 (s, 1H, NC*H*N), 9.71 (d, 1H, $^3J_{H-H}$ = 5.5 Hz, 6-*H* of Py), 8.43–8.33 (m, 2H, 3,5-*H* of Py), 7.75 (t, 1H, $^3J_{H-H}$ = 6 Hz, 4-*H* of Py), 4.29 (s, 3H, C*H*$_3$). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 199.52, 192.48 (*C*O), 187.47 (Ru–*C*), 157.58, 155.84, 141.15, 140.34, 125.79, 111.90 (N*C*HN and Py–*C*), 34.87 (*C*H$_3$). *Anal.* Calc. for $C_{10}H_8N_4O_2Cl_2Ru$: C, 30.94; H, 2.08; N, 14.43. Found: C, 30.96; H, 2.25; N, 14.43%. FT-IR (KBr, cm^{-1}): ν_{CO} 2059 and 1953 cm^{-1}.

2.3. X-ray crystal structure determination

Crystals suitable for X-ray diffraction study were obtained by slow evaporation of solutions of the complexes in CH_2Cl_2. Diffraction data were measured on a Bruker SMART CCD diffractometer with graphite monochromated Mo Ka radiation (λ = 0.71073 Å) at 298 K. Absorption corrections were applied using SADABS program [52]. The structures were solved by direct methods and refined by full-matrix least-squares refinement using the SHELXL-97 program [53] package. The hydrogen atoms were positioned in idealized positions and refined in the riding-model approximation. Other non-hydrogen atoms were refined with anisotropic thermal parameters. Crystal data collection and structure refinement parameters were listed in Table 2.

2.4. General method for catalytic hydrogen transfer reactions

The hydrogen transfer reactions were carried out in a closed Schlenk flask under inert atmosphere. To a solution of KOH (0.02 M) in 10 ml of 2-propanol were added a ruthenium complex (8 μmol) and acetophenone (2 mmol). The mixture was heated to 82 °C with stirring under nitrogen. Progress of the reaction was monitored by GC.

3. Results and discussion

3.1. Synthesis of carbene precursors and NHC ruthenium(II) complexes

The 1,2,4-triazolium salt **L5** was prepared by the alkylation of 4-(2-pyridyl)-1,2,4-triazole with excess iodomethane in acetone. The ^{1}H NMR spectrum of the triazolium salt **L5** displays two singlets at δ = 10.96 (CH$_3$NC*H*N) and 9.99 (NC*H*N) ppm, which are characteristic of a triazolium precursor. Two resonances (δ = 144.81 and 139.99 ppm) of **L5** in the ^{13}C NMR spectrum are attributed to CH$_3$NCHN and NCHN carbon atoms, respectively.

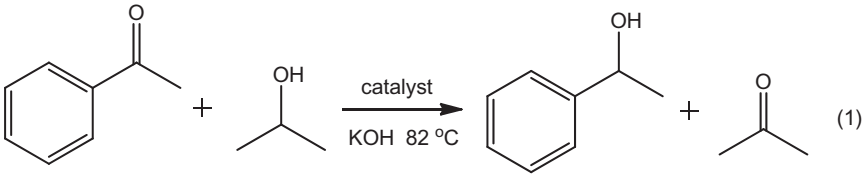
Ruthenium complexes **1a**, **1b**, **2a**, **2b**, **4a**, **4b**, **5a** and **5b** were synthesized by the silver–carbene transmetallation method [54] (Scheme 1). The ligand precursors **L1**, **L2**, **L4** and **L5** were treated with Ag_2O in CH_2Cl_2 or MeOH at room temperature to give silver N-heterocyclic carbene compounds. Subsequent addition of $[Ru(CO)_2Cl_2]_n$ formed the corresponding Ru carbene complexes as structural isomers, which were separated by column chromatography. However, the reaction of a mixture of **L3**, Ag_2O and $[Ru(CO)_2Cl_2]_n$ in CH_2Cl_2 or MeOH failed to give the desired product. Instead the reaction gave products that were difficult to separate. Replacing the base Ag_2O with NEt_3 led to a cleaner product formation, and purification by recrystallization afforded only one product (**3b**) as a light-yellow solid (Scheme 1).

The ^{1}H NMR spectra of these complexes showed the disappearance of the imidazolium C_2–H, benzimidazolium C_2–H and 1,2,4-triazolium C_5–H proton signals of ligand precursors in the low field, indicating that carbene carbon atom coordinates to the Ru atom. The carbene carbon resonances (δ = 175.18–190.53 ppm) of these complexes in the ^{13}C NMR spectra were found in the expected range [55–58,28]. The ^{1}H NMR spectra of the ruthenium complexes reported by Cheng et al. show that the chemical shifts of 6-H in the pyridine ligands for trans(Cl)-cis(CO) ruthenium complexes are lower than those of corresponding cis(Cl)-cis(CO) ruthenium complexes. Thus we speculate, from comparing the ^{1}H NMR spectra of our complexes, that the structures of **1a**, **2a**, **4a** and **5a** are *trans*(Cl)–*cis*(CO) and the conformation of **1b**, **2b**, **3b**, **4b** and **5b** are *cis*(Cl)–*cis*(CO).

These ruthenium complexes are stable in the solid state when exposed to air. The dichloromethane or methanol solution of complexes **1a**, **2a**, **5a** and **5b**, however, turned from yellow to dark green after a few days in the air, whereas the solution of **1b**, **2b**, **3b**, **4a** and **4b** in dichloromethane or methanol are stable in air.

The IR spectra of these complexes show two intense absorption bands in the range 2044–2062 and 1953–1996 cm^{-1}, which are assigned to the stretching vibrations of the two carbonyl ligands.

The coordination of Py-NHC ligands in **1b**, **2b**, **3b** and **4b** have been confirmed by crystallographic studies. Unfortunately no suitable crystals for crystallographic studies have been obtained for either **5a** or **5b**. When we tried to crystallise **5b** in CH_3CN, a new complex with a CH_3CN ligand, {[1-methyl-4-(2-pyridyl)-1,2,4-triazoline-5-ylidene]Ru(CO)(CH$_3$CN)Cl$_2$} (**5bb**), was obtained. Its structure was determined by crystallographic study (see Supplementary materials Fig. 1S, Tables 1S and 2S), in which the C5 carbon of the Py-NHC ligand is coordinated to the ruthenium center. It



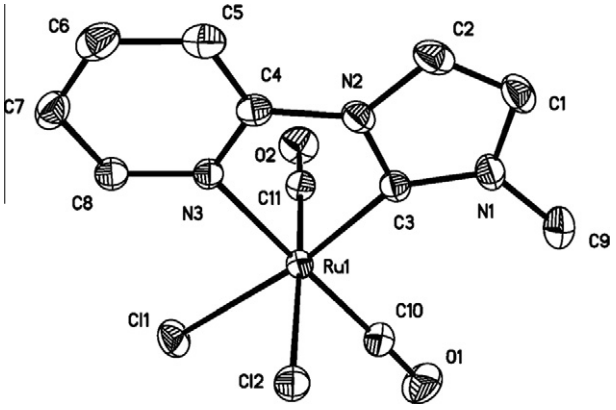


Fig. 1. Molecular structure of complex **1b** with ellipsoids drawn at 30% probability level. Hydrogen atoms and solvent (CH_2Cl_2) have been omitted for clarity.

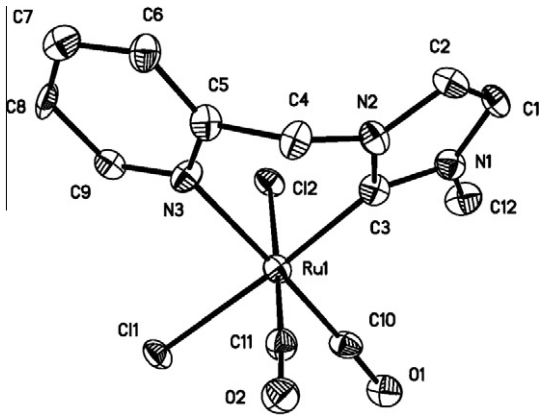


Fig. 2. Molecular structure of complex **2b** with ellipsoids drawn at 30% probability level. Hydrogen atoms and solvent (CH_2Cl_2) have been omitted for clarity.

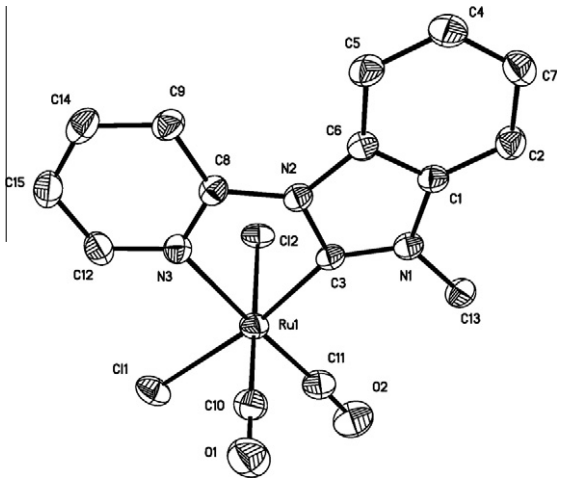


Fig. 3. Molecular structure of complex **3b** with ellipsoids drawn at 30% probability level. Hydrogen atoms have been omitted for clarity.

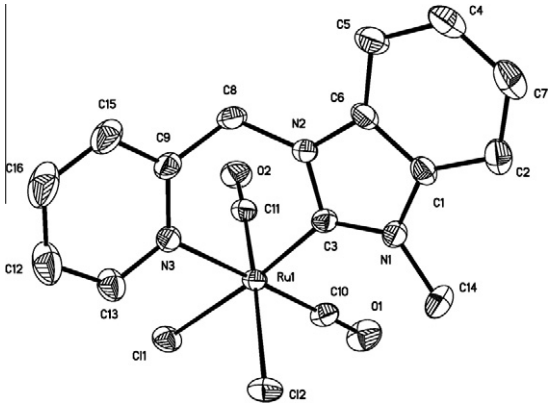


Fig. 4. Molecular structure of complex **4b** with ellipsoids drawn at 30% probability level. Hydrogen atoms have been omitted for clarity.

is reasonable to assume that in the conversion of **5b**–**5bb**, the coordination of Py-NHC is kept constant. Therefore we reasoned that the Py-NHC ligand binds to the Ru atom via the normal C5, not the C3 atom.

3.2. Molecular structures of *1b*, *2b*, *3b* and *4b*

Ruthenium(II) complexes **1b**, **2b**, **3b** and **4b** were structurally characterized by single-crystal X-ray diffraction. Single crystals of **1b**·1/2CH_2Cl_2, **2b**·1/2CH_2Cl_2, **3b**, and **4b** were obtained by slow evaporation of dichloromethane solutions of the complexes. CH_2Cl_2 (1/2 equiv.) is cocrystallised in the crystals of **1b** and **2b**. The molecular structures and selected bond lengths (Å) and bond angles (°) of **1b**, **2b**, **3b** and **4b** are depicted in Fig. 1–4 and Table 1, respectively. X-ray crystallographic data and structure refinement parameters are given in Table 2. The central ruthenium atoms in **1b**, **2b**, **3b** and **4b** are coordinated by the carbene carbon and pyridine nitrogen atoms from the ligand, together with two chlorides and two CO ligands, leading to a slightly distorted octahedron geometry. Both the two chlorides atoms and CO ligands are *cis*-positioned, with one of the chlorides *trans* to the carbene carbon atom and one of the CO groups *trans* to the pyridine nitrogen atom.

The Ru–$C_{carbene}$ distances of 2.014(3) (Å) (**1b**), 2.006(5) (Å) (**2b**), 2.002(3) (Å) (**3b**), and 2.029(2) (Å) (**4b**) fall in the expected range observed for other known Ru-NHC complexes [41,42,59,60]. The bond lengths of Ru–$N_{pyridine}$ in **1b**, **2b**, **3b** and **4b** are in the range of 2.132(3)–2.172(4) (Å), which are similar to the Ru-N distances observed in the reported ruthenium complexes containing Py-NHC ligands [2.014(5)–2.172(3) Å] [32,44]. The bond distances Ru–CO [1.874(3) and 1.878(3) (Å) for **1b**], [1.859(5) and 1.869(5) (Å) for **2b**], [1.891(4) and 1.884(4) (Å) for **3b**] and [1.866(3) and 1.853(3) (Å) for **4b**] are consistent with typical Ru–CO lengths of the reported ruthenium(II) carbonyl complexes [61–63]. The average Ru–Cl distance is 2.452 Å.

The imidazole and benzimidazole ring in **1b** and **3b**, respectively, is approximately coplanar with the pyridine ring. In **2b** and **4b**, they form a dihedral angle (51.91° and 60.28°), respectively. The $C_{carbene}$–Ru–$N_{pyridine}$ bond angles in the five-membered chelating ring of **1b** [77.51(10)°] and **3b** [77.40(12)°] are smaller than those in the six-membered rings of **2b** [85.86(17)°] and **4b** [84.55(8)°], which may be due to the influence of the methylene bridge.

3.3. Catalytic transfer hydrogenation of ketones

Several ruthenium(II) complexes [41,42] of N-heterocyclic carbenes are effective catalyst precursors for the transfer hydrogenation of ketones. Only a few NHC ruthenium(II) complexes containing imidazole ring carbenes have been used as active catalysts in this reaction [30,64]. Catalytic activities of NHC ruthenium(II) complexes with benzimidazole and triazole ring carbenes have not been studied. We have investigated and compared the catalytic properties of ruthenium(II) complexes of NHC containing an imidazole (**1** and **2**), benzimidazole (**3** and **4**) and triazole (**5**) ring in the transfer hydrogenation of acetophenone.

We chose the reduction of acetophenone to 1-phenylethanol by 2-propanol as a model reaction (Eq. (1)). The catalytic experiments were carried out at 82 °C using acetophenone (2 mmol), Ru complexes (8 μmol) and KOH (0.02 M) in 10 ml of 2-propanol. The conversion was monitored by GC.

The conversion versus reaction time plots are shown in Fig. 2S (Supplementary materials; Three measurements for each data point). The conversion versus reaction time plots as an average of three measurements are shown in Fig 5. Complexes **1**, **3**, and **5** are more active than **2** and **4**, implying that the presence of a methylene group between pyridine ring and N-heterocycle is not beneficial for the catalytic transfer hydrogenation of acetophenone, which is consistent with the previous report of Cheng et al. [30]. By comparing the catalytic results of the ruthenium complexes without a methylene bridge we find that catalytic behaviors of **1**

Table 2
X-ray crystallographic data and structure refinement parameters for complexes **1b**, **2b**, **3b**, and **4b**.

Compound	**1b**·0.5CH_2Cl_2	**2b**·0.5CH_2Cl_2	**3b**	**4b**
Formula	$C_{11}H_9Cl_2N_3O_2Ru$·0.5CH_2Cl_2	$C_{12}H_{11}Cl_2N_3O_2Ru$·0.5CH_2Cl_2	$C_{15}H_{11}Cl_2N_3O_2Ru$	$C_{16}H_{13}Cl_2N_3O_2Ru$
Formula weight	429.65	443.67	437.24	451.26
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2(1)/*n*	*C*2/*c*	*P*21/*c*
Crystal dimensions (mm)	0.28 × 0.23 × 0.21	0.28 × 0.22 × 0.20	0.28 × 0.24 × 0.22	0.28 × 0.24 × 0.22
a (Å)	25.8224(18)	9.4233(11)	17.381(2)	9.8632(7)
b (Å)	9.7623(7)	15.9549(18)	14.585(2)	11.0026(7)
c (Å)	12.7567(9)	10.8236(13)	13.9465(19)	16.2889(11)
α (°)	90	90	90	90
β (°)	108.0890(10)	102.647(2)	114.497(2)	99.4240(10)
γ (°)	90	90	90	90
V (Å^3)	3056.8(4)	1587.8(3)	3217.2(7)	1743.8(2)
D_{calc} (Mg/m^3)	1.867	1.856	1.805	1.719
Z	8	4	8	4
Radiation (Mo Kα)	0.71073	0.71073	0.71073	0.71073
F(000)	1688	876	1728	896
Absorption coefficient (mm^{-1})	1.554	1.499	1.318	1.218
θ range for data collection (°)	1.66–26.0	2.31–26.0	1.9–26.0	2.09–26.0
Data/restraints/parameters	2995/0/186	3119/0/200	3144/0/209	3430/4/218
Reflections collected	8111	8591	8555	9296
Reflections unique	2995	3119	3144	3430
R_{int}	0.0645	0.0355	0.0183	0.0575
Goodness-of-fit (GOF) on F^2	1.060	1.022	1.046	1.075
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0288, 0.0763	0.0452, 0.1063	0.0305, 0.1018	0.0244, 0.0537
R_1, wR_2 (all data)	0.0325, 0.0782	0.0558, 0.1093	0.0377, 0.1061	0.0314, 0.0549
Largest differences in peak and hole (e Å^3)	0.616, −0.772	0.948, −0.989	0.836, −0.363	0.331, −0.494

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

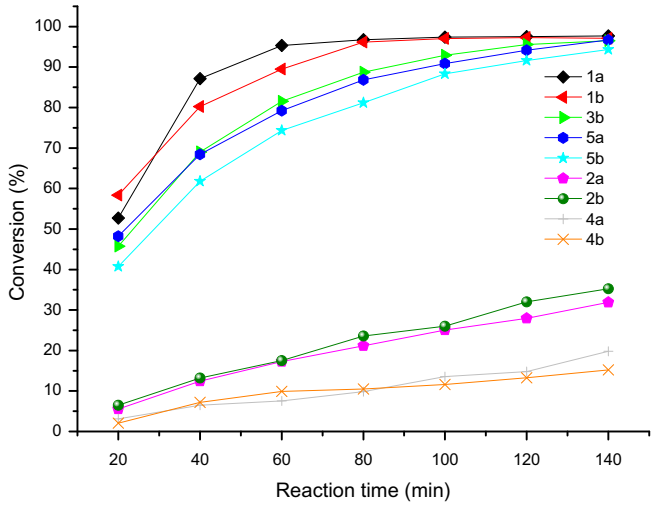
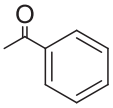
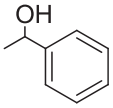
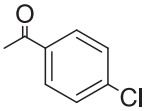
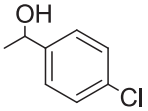


Fig. 5. Conversion vs. reaction time of the catalytic transfer hydrogenation of acetophenone with ruthenium(II) complexes as catalysts.

containing an NHC ligand with an imidazole ring are the best among the three types of N-heterocycle carbenes. The catalytic activity of **3** containing a benzimidazole ring is slightly higher than those of **5** bearing a triazole ring, suggesting that electronic effect exerts an influence on catalytic properties. The catalytic performance of complexes decreases **1** > **3** > **5** while the σ-donor ability decreases in the order imidazole > benzimidazole > 1,2,4-triazole. In **2** and **4** with a methylene bridge, we have also observed the same trend that catalytic behaviors of **2** with an imidazole ring are more active than those of **4** containing benzimidazole, respectively.

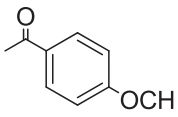
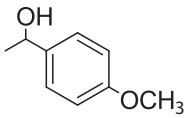
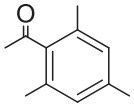
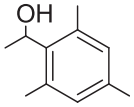
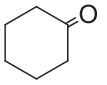
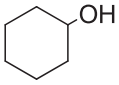
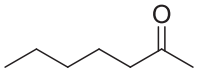
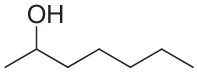
Complex **1a** is the most efficient in transfer hydrogenation reaction, and the conversion is 95% in 1 h. Therefore we use **1a** as the catalyst to study the transfer hydrogenation of other ketones. The reactions are performed under the same conditions as above (Table 3). **1a** displays considerable activity in the transfer hydrogenation of cyclohexanone (99% conversion after 1 h, entry 5). For acetophenone, 4-chloro acetophenone and 2-heptanone, the activity of **1a** is almost comparable: 97% conversion after 2 h (entry 1), 97% conversion after 2 h (entry 2), and 96% conversion after 2 h (entry 6). In the case of 4-methoxyacetophenone, **1a** has a moderate activity (79% conversion after 2 h, entry 3), while in the reduction of 2,4,6-trimethyl acetophenone **1a** shows a low catalytic

Table 3
Catalytic transfer hydrogenation of ketones using **1a**.[a]

Entry	Ketone	Alcohol	Time (h)	Conversion (%)[b]
1			1	95
			2	97
2			1	96
			2	97

(*continued on next page*)

Table 3 (*continued*)

Entry	Ketone	Alcohol	Time (h)	Conversion (%)[b]
3			1 2	72 79
4			1 2	35 36
5			1 2	99 100
6			1 2	91 96

[a] Reaction condition: reactions were carried out at 82 °C; ketone (2 mmol), Ru complex **1a** (8 μmol), KOH (0.02 M) in 10 ml 2-propanol; ketone/Ru/KOH = 1000/4/100.
[b] The conversion was determined by GC.

activity (36% conversion after 2 h, entry 4) which may arise from steric bulk of the substrate.

4. Conclusions

A series of ruthenium(II) complexes with three types of pyridine-functionalised NHC ligands based on imidazole, benzimidazole and triazole groups have been prepared and characterized. The X-ray diffraction studies confirm that the structures of **1b**, **2b**, **3b** and **4b** are *cis*(Cl)–*cis*(CO).

The catalytic activities of these complexes have been studied in the transfer hydrogenation, revealing that **1a** has excellent catalytic properties in the transfer hydrogenation of acetophenone. Ruthenium complexes without a methylene group bridge **1** (**1a** and **1b**), **3** (**3b**), and **5** (**5a** and **5b**) are more active than **2** (**2a** and **2b**) and **4** (**4a** and **4b**) with a methylene group bridge. The catalytic performance of analogous complexes, **1** (**1a** and **1b**) > **3** (**3b**) > **5** (**5a** and **5b**), decreases when the σ-donor ability decreases in the order imidazole > benzimidazole > 1,2,4-triazole, and the catalytic activities of **2** (**2a** and **2b**) are higher than **4** (**4a** and **4b**). It is evident that the imidazole systems offer the most favorable electronic properties and thus the highest activity.

Acknowledgments

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Appendix A. Supplementary material

CCDC 825041, 825042, 825043, 825044 and 840555 contain the supplementary crystallographic data for complexes **1b**, **2b**, **3b**, **4b** and **5bb**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Molecular structure (Fig. 1S), summary of crystallographic data (Table 1S), bond lengths and bond angles (Table 2S) for **5bb**, and Fig. 2S giving the conversion vs. reaction time plots (Three measurements for each data point). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.09.009.

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