Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Dalton Transactions

RSCPublishing

PAPER

Donor Functionalized Ruthenium *N*-Heterocyclic Carbene Complexes in Alcohol Oxidation Reactions

Abbas Raja Naziruddin, Chun-Shiuan Zhuang, Wan-Jung Lin and Wen-Shu Hwang*

Cite this: DOI: 10.1039/x0xx00000x

Received 00th November 2013,
Accepted 00th XXX 201X

DOI: 10.1039/x0xx00000x

www.rsc.org/

N-pyridyl, *N'*-amido functionalized imidazolium bromides were obtained in high yields as *N*-heterocyclic carbene (NHC) precursor and used as bidentate or a pincer ligands to obtain ruthenium complexes *via* silver NHC transmetallation route. Incorporation of a phenyl group as an amido-*N* substituent (*R* = Ph) results in bidentate coordination mode through C_{NHC} and the $N_{pyridyl}$ donors, whereas in its absence (*R* = H) a pincer coordination mode was observed through $N_{pyridyl}$^C_{NHC}^O_{amido} donors. Ruthenium complex featuring pincer type NCO coordination mode with a protic *NH* function adjacent to the coordinating O_{amido} atom was found to efficiently catalyse the oxidation of activated alcohols effecting quantitative conversions within 30 minutes. However oxidation of deactivated alcohols required longer reaction times to effect the quantitative transformation.

INTRODUCTION

Excellent catalytic activity and high robustness of metal–*N*-heterocyclic carbene (NHC) complexes along with their simple preparation from readily available azolium precursors as well as their ability to catalyse diverse array of organic reactions have propelled substantial development in transition metal mediated organic transformations over the past two decades.[1] Steric and electronic tuning of NHC ligands can be achieved through the *N*-wingtip functionalization or through the backbone modification[2] to obtain highly selective organometallic catalyst,[3] OLED materials[4] or molecules with anticancer activities.[5] *N*-donor functionalized NHC wingtips combine the structural aspects of NHC ligands along with that of hetero atom group in these hybrid bidentate[3b, c, 6] or tridentate[7] donor sets. Complexes bearing NHC ligands functionalized with heterocyclic groups including pyridine,[8] pyrazine,[9] pyrimidine,[8a, 8f, 10] quinoline,[11] benzimidazole,[12] oxazoline,[13] phenanthroline,[14] are significantly studied over the last few years. In-addition to *N*-donor functionalized NHC ligands; few reports also describe the direct oxidative insertion of the alkyl wingtip to the ruthenium center with the formation of chelate complexes.[15]

A special class of weakly coordinating ligands act as hemilabile donors, which upon coordination to catalytically active metal center exhibit co-operative effects.[16] Mixed chelate complexes feature the coordinated NHC ligand intact whereas a reversible de-coordination and coordination of linked hemilabile moiety promote the substrate binding and the product dissociation steps of the catalytic cycle to exhibit co-operativity.[17] Even though such cooperative catalyses are well established in hemilabile groups linked to phosphine donors *via* phenylene bridges in a pincer type coordination mode,[18] such occurrences involving NHCs donors are relatively rare.[19] Silver or gold complexes bearing NHC ligands functionalized with hemilabile amido group in the *N*-wingtip are previously known.[20] Few ruthenium[21] or iridium[22] NHC complexes bearing hemilabile *O*-donor have also been previously employed in transfer hydrogenation reactions, whereas palladium complexes with *S*-functionalized NHCs in pseudo pincer fashion were employed in intermolecular hydroamination reactions.[17]

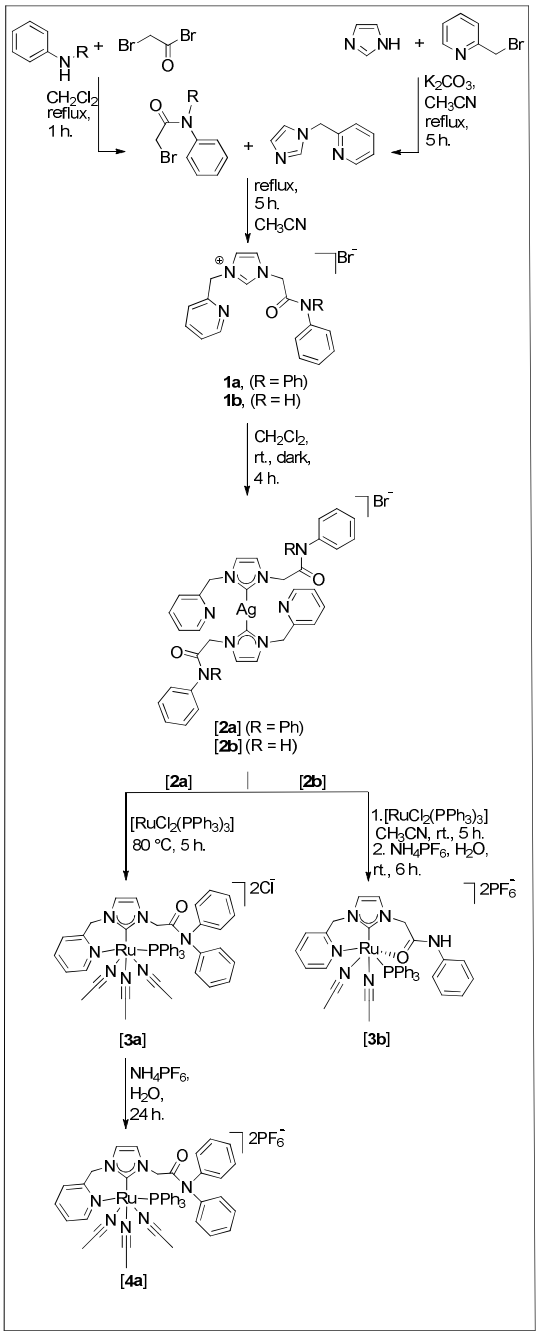
The oxidation of alcohols to the corresponding aldehydes or ketones is one of the key steps in conventional organic transformations including natural product synthesis.[23] Although a variety of methods have been developed for this purpose, most of them employ rather harsh reaction conditions and require stoichiometric amounts of oxidant generating undesirable coproduct, that eventually result in unselective transformations.[24] Aerobic oxidations of alcohols using metal free,[25] homogeneous[25-26] or heterogeneous[24c, 26e, 27] transition metal catalysts have been previously developed, but most of these reactions require the addition of large amounts of base, heating, or pressured oxygen. Due to the importance of this transformation in organic synthesis, the development of efficient oxidation processes under milder conditions are highly desirable.[26h, 28]

Several ruthenium complexes have been studied as catalysts for oxidation of alcohols.[26e, 29] In this work, we report three new ruthenium complexes of potential chelating ligands, featuring an *N*-donor of the pyridyl wingtip and an *O*-donor of the amide wingtips linked to the central NHC precursor. Our interest in these ligand system emerge from the fact that metal complexes with amido functionalized NHC ligands are rare and to the best of our knowledge, this is the first report of ruthenium complexes featuring amide/pyridyl functionalized NHC ligands. In addition we have evaluated the use of these complexes as precatalyst towards alcohol oxidation reactions.

RESULTS AND DISCUSSION

Synthesis of ligand precursors and complexes are outlined in Scheme 1. Ligand precursors **1a** and **1b** were obtained in high yields by heating equimolar stoichiometric amounts of 2-imidazol-1-ylmethyl-pyridine and 2-bromo-*N*,*N*-diphenyl-acetamide or 2-bromo-*N*-phenyl-acetamide in acetonitrile under reflux conditions for 6 h. The ^{1}H NMR spectrum of **1a** exhibited a sharp downfield resonance at δ 9.89 ppm, for NC*H*N imidazolium proton, while the ^{1}H NMR of spectrum of **1b** revealed two such downfield signals at δ 10.65 and 9.71 ppm, corresponding to the N*H* and NC*H*N imidazolium protons respectively. NMR data of **1a** and **1b** are in comparable range to those of similar imidazolium NHC precursors.[30] Reaction of **1a** or **1b** with Ag_2O in dichloromethane under exclusion of light at ambient temperature resulted in the formation of Ag–NHC complexes **2a** or **2b** within 4 h. Ruthenium–NHC complex **3a** was obtained in good yields (80.7%) *via* standard *transmetallation* reaction of complex **2a** with $[Ru(PPh_3)_3Cl_2]$ in acetonitrile under refluxion in 5 h. **3a** was further subjected to counter ion exchange by reacting with NH_4PF_6 in an aqueous solution at ambient temperature to yield **4a**. Similar to the synthesis of **3a**, the ruthenium complex **3b** was also obtained from direct *transmetallation* reaction of **2b** with $[Ru(PPh_3)_3Cl_2]$ in CH_3CN at ambient temperature in 5 h, the chloride salt thus obtained was also subjected to an anion exchange reaction using NH_4PF_6 resulting in the formation of the pincer complex **3b** with PF_6 counter ions.

All the ligand precursors and ruthenium complexes are characterized by standard analytical techniques. ^{1}H NMR spectra of all complexes are devoid of NC*H*N imidazolium proton resonances and ^{13}C NMR spectra exhibited characteristic carbenoid carbon atom resonance around $\delta \sim 180$ ppm, confirm the coordination of carbene ligand in **2a**, **2b**, **3a**, **3b** and **4a**. ^{31}P NMR spectra of complexes **3a**, **4a**, and **3b** exhibited the coordinated phosphorus resonances around δ 45–48 ppm.[31] The methylene bridges linking the pyridyl and the amide donor to the central NHC ligand in **3a**, **4a**, and **3b** exhibited four sets of doublet resonances in the range of δ 6.1–5.4 and 4.3–2.9 ppm with a coupling constant of J_{H-H} ~16 Hz due to the diastereotopicity of methylene protons arising due to complexation.[32] IR spectra of complexes **2a**, **2b**, **3a** and **4a** displayed an amide C=O stretching band at 1675–1693 cm^{-1}, while **3b** exhibited a large lowering of this stretching frequency to 1621 cm^{-1}, due to the coordination of the oxygen atom to the ruthenium center. All complexes reported in this work were observed to be air and moisture stable.



Scheme 1 Synthesis of *N-O* functionalized NHC ligand precursors and their ruthenium complexes *via* silver NHC transmetallation route.

Single crystals suitable for X-ray diffraction analyses were obtained by slow diffusion of diethylether into a CH_3CN solution of **4a** or by slow evaporation of CH_2Cl_2 solution of **3b.** Crystal data and refinement parameters are listed in Table S1 (ESI).

Dalton Transactions RSCPublishing

PAPER

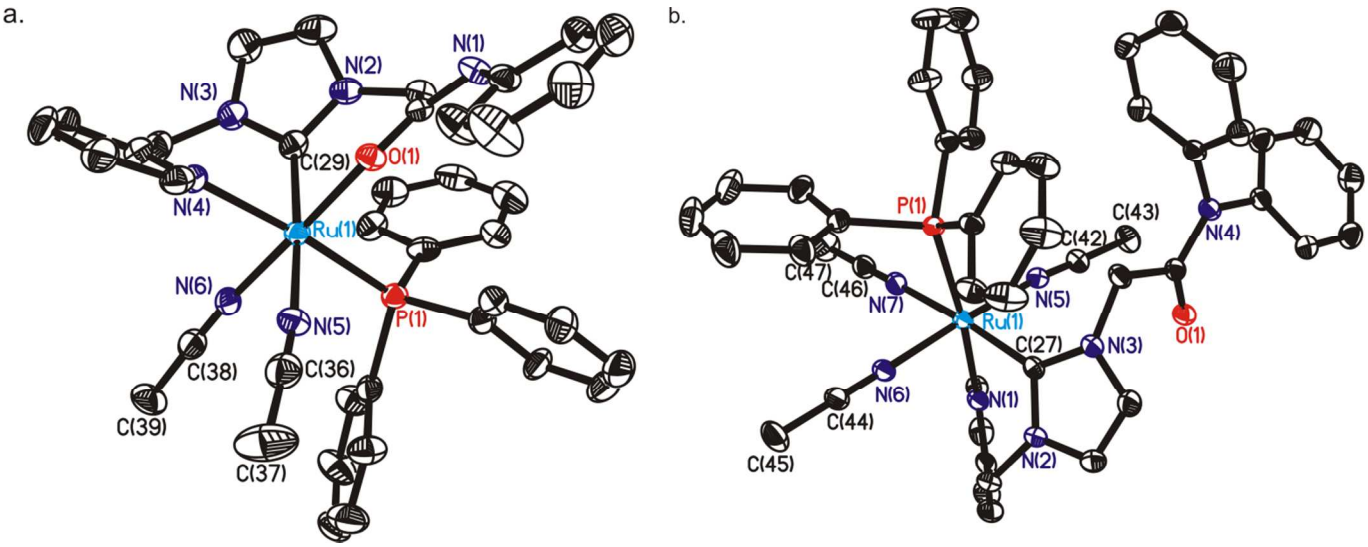


Fig 1. a. Molecular structure of **3b**. **b.** Molecular structure of **4a**. Hydrogen and PF_6 anion are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) of **3b** and **4a**

3b		**4a**	
Ru(1)—C(29)	1.978(6)	Ru(1) –C(27)	2.033(3)
Ru(1)—N(4)	2.147(5)	Ru(1) –N(1)	2.148(3)
Ru(1)—P(1)	2.317(2)	Ru(1) –P(1)	2.352(2)
Ru(1)—O(1)	2.143(4)	Ru(1) –N(5)	2.029(3)
Ru(1)—N(5)	2.113(6)	Ru(1)—N(6)	2.028(3)
Ru(1)—N(6)	1.994(5)	Ru(1) –N(7)	2.102(3)
C(25)—O(1)	1.244(7)	C(29) –O(1)	1.213(4)
C(29)—Ru(1)—N(5)	169.90(2)	C(27) –Ru(1) –N(7)	172.48(12)
N(4) –Ru(1)–P(1)	173.50(14)	N(1)–Ru(1)–P(1)	174.51(8)
N(6)–Ru(1)–O(1)	176.02(21)	N(5)–Ru(1)–N(6)	175.25(11)
C(29)–Ru(1)–N(4)	81.69(24)	C(27)–Ru(1)–N(1)	83.96(12)
O(1)–Ru(1)–N(4)	90.19(17)	N(6)–Ru(1)–N(7)	87.81(11)
N(5)–Ru(1)–N(6)	85.75(24)		

Dalton Transactions RSCPublishing

PAPER

Selected bond lengths and angles are summarized in Table 1. Molecular structure of **4a**, depicted in Fig. 1b, shows the *N*/*O*-functionalized NHC ligand **1a** (R = Ph) coordinates to the ruthenium center through the carbenoid–*C* and the pyridyl–*N*, donors with Ru(1)–C(27) and Ru(1)–N(1) bond lengths measuring 2.033(3) and 2.148(3) Å, respectively to form a six-membered chelate ring with a bite angle of 83.96(12). The PPh_3 ligand occurs in a *trans* configuration to the pyridyl–*N* atom, featuring Ru(1)–P(1) bond distance of 2.352(2) Å. The octahedral coordination sphere of ruthenium center is completed by three CH_3CN ligands with first two Ru–N bond distances measuring 2.028(3) and 2.029(3) Å, whereas the third Ru–N bond that occur *trans* to the NHC ligand is relatively elongated 2.102(3) Å. In addition, bond angles of three *trans* donor pairs across the ruthenium center, C(27)–Ru(1)–N(7), N(1)–Ru(1)–N(6), and N(5)–Ru(1)–N(6) were observed to be 172.48(12), 174.51(8), and 175.25(11)°, respectively. The bonding parameters around the ruthenium center confirm a slightly distorted octahedral geometry and are in a comparable range to those of closely related ruthenium complexes in the literature.[33]

Molecular structure of **3b**, as depicted in Fig. 1a, also confirms a distorted octahedral geometry around the ruthenium center. The *N*/*O*-functionalized mixed NHC donor **1b** (R = H) act as a *terdentate* pincer ligand exhibiting an additional weak coordination through the oxygen atom. One of the weakly bound CH_3CN in **4a**, is substituted by a C=O donor of an amide functionalized *N*-wing tip featuring a Ru–O bond distance of 2.143(4) Å. The ruthenium pincer complex **3b** exhibit a shorter Ru–C_{NHC} bond distance of 1.978(6) Å, relative to that observed in **4a**. Indeed upon coordination of the amide carbonyl (O) donor to the ruthenium center, the C=O bond distance was elongated to 1.244(7) Å in **3b**, from 1.213(4) Å in **4a**. This data is also commensurate with the C=O stretching frequency observed from the IR spectrum. Two CH_3CN ligands are observed in a mutually *cis* configuration with Ru–N bond distances measuring 2.113(6) Å (*trans* to C_{NHC}) and 1.994(5) Å (*trans* to $O_{C=O}$).

Ruthenium complexes reported herein were evaluated towards catalytic oxidation of alcohol to the corresponding aldehyde or ketone. Our optimization experiments confirmed that a combination of KO^{t}Bu, toluene and 5 mol% ruthenium pre-catalyst at reaction temperature of 100 °C afforded the best result for catalytic oxidation of benzyl alcohol. Furthermore, we do not observe any over oxidation of the aldehyde to the carboxylic acid. The standard oxidation experiment was thus performed on benzyl alcohol (2.0 mmol) using the ruthenium pre-catalysts (5.0 mol %) and KO^{t}Bu (1.0 mmol) in toluene (5 mL) at 100 °C. Product yields were monitored by GC.

Catalytic results for the oxidation of benzyl alcohol using **3a**, **4a**, and **3b** are summarized in Fig. 2. Reaction profiles show that **3a**, **4a**, and **3b** demonstrate very good activity towards catalytic oxidation of benzyl alcohol resulting in almost quantitative formation of benzaldehyde within 100, 50, and 25 min respectively. Complexes **3a** and **4a** bearing three CH_3CN ligands could facilitate a facile release of the labile CH_3CN ligands to generate vacant site for the incoming deprotonated benzyl–alkoxide moiety to initiate the catalytic reaction and further propel the subsequent *β*-hydrogen elimination reaction to furnish the carbonyl product. A comparison of reaction profiles of **3a** *vs*. **4a** also supports strong counter ion effect that significantly influences the results of catalytic conversion. However, **3b** with only two CH_3CN ligands and a labile *O*-donor *via* the NHC wingtip, exhibited even better activity than **3a** or **4a**; we speculate that *N*-wing tip substituent on the NHC ligand bearing less sterically hindered amide–*O* donor along with the protic *NH* function lying adjacent the weakly coordinating oxygen atom could contribute to the enhanced activities of **3b**.

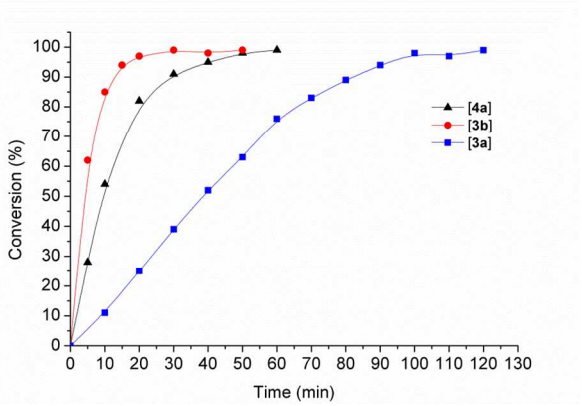


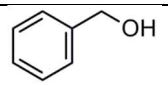
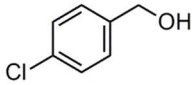
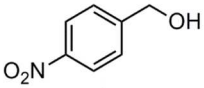
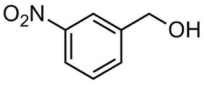
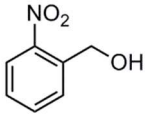
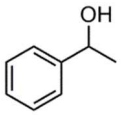
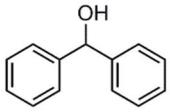
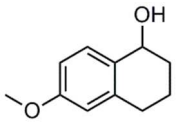
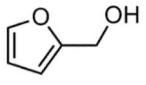
Fig. 2 Reaction profiles for the oxidation of benzyl alcohol (2.0 mmol) to benzaldehyde with Ru(II) precatalysts **3a**, **4a** and **3b** (5.0 mol%) in toluene (5 mL) in the presence of KO^{t}Bu (1.0 mmol) at 100 °C. Catalytic conversions of the standard benzyl alcohol substrate were monitored by GC.

Post-catalytic analysis of **3b** and **4a** was conducted to study the stabilizing effect of the chelating *N*/*O* functionalized NHC and phosphine ligands in catalytic reaction. After the completion of the catalytic reaction, the reaction mixture was extracted in an ether/water system. The organic phase was separated and the aqueous layer was decanted. The residue was dissolved in acetonitrile and the solution was filtered. The filtrate was further dried *in vacuo* and the residue was subjected to NMR and IR analyses. Results confirmed that the *N*/*O* functionalized NHC ligand as well as the phosphine ligand remains intact at the ruthenium center in **3b** and **4a**.

To investigate the tolerance of substituent functionality on benzyl alcohol and study the generality of the current catalytic system towards activated or unactivated alcohols few selected substrates were screened for catalytic reactions using **3b** and **4a** under optimized conditions. Although the pre-catalysts **3b** and **4a** afforded almost quantitative conversion for activated aromatic alcohols and unactivated alcohols within 30 minutes and 3 ~ 8 h, respectively, a relative study of catalytic activities of **3b** and **4a** in 30 minutes are tabulated in Table 2. Indeed, an expected trend of higher conversions for activated alcohols using both the pre-catalysts **3b** and **4a** was observed. As evident from the entries 1 and 6, conversion of phenylmethanol or 1-phenylethanol occurred almost quantitatively with the precatalyst **3b** (99–98%); whereas the conversion was slightly lowered upon using **4a** as the precatalyst (91–90%). With a *p*-chloro substituent on the phenyl ring (entry 2) higher yields of the corresponding aldehyde (95%) was observed upon using the precatalyst **4a**, while almost quantitative conversions upon using **3b** was retained (99%).

We also tested the effect of catalytic conversions upon introducing an electron withdrawing substituent (NO_2) at *p*- (entry 3), *m*- (entry 4) or *o*- (entry 5) positions of the phenylmethanol substrates. In all cases the isolated yields at the end of 30 minutes were observed from moderate to poor; however the precatalyst **3b** was relatively more efficient for such oxidation of deactivated aromatic alcohols. The pre-catalyst **3b** effected 65%, 45% and 30% conversion of (*p*-NO_2)-phenylmethanol, (*m*-NO_2)-phenylmethanol and (*o*-NO_2)-phenylmethanol respectively. Especially the poor yields in the oxidation of (*m*-NO_2)-phenylmethanol, could arise from mixed factor of steric and electronic effects as well as the occurrence of intramolecular hydrogen bonding between the nitro and hydroxyl groups that considerably deactivates the substrate. However such substrates usually require prolonged reaction time over 20 h to yield quantitative conversions.[34] Secondary alcohol substrates like diphenylmethanol, 6-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol (entries 7 and 8) underwent good conversions with the precatalyst **3b** (95–93%) and **4a** (88–85%). Previously an *in situ* generated Cu–NHC–TEMPO catalyst took 15 h to effect the oxidation of furan-2-ylmethanol with 71% conversions.[34] Precatalyst **3b** facilitated a slight improvement of this catalytic yield (entry 9) (76%), however in a remarkably shorter reaction time (30 min.).

Table 2 Results of oxidation of different alcohols catalyzed by **4a** and **3b** in 30 min.[a]

Entry	Alcohol (Substrate)	Catal.	yield %[b]
1		**3b**	99
		4a	91
2		**3b**	99
		4a	95
3		**3b**	65 (97 in 3.0 h)
		4a	45 (98 in 4.5 h)
4		**3b**	45 (96 in 4.5 h)
		4a	29 (99 in 7.0 h)
5		**3b**	30 (97 in 7.0 h)
		4a	12 (95 in 8.0 h)
6		**3b**	98
		4a	90
7		**3b**	95
		4a	88
8		**3b**	93
		4a	85
9		**3b**	76 (96 in 2.5 h)
		4a	59 (97 in 4.0 h)

[a] Reaction conditions: 2.0 mmol alcohol, 1.0 mmol KO-^{t}Bu, and 5.0 mol% precatalyst in 5 mL toluene at 100 °C in 30 min.
[b] Isolated yields

SUMMARY

In conclusion, we have prepared a new amide functionalized NHC ligand precursor, that coordinates to the ruthenium center in either bidentate or pincer coordination modes, leading to a distorted octahedral geometry around the metal center. Amongst three new ruthenium complexes reported herein, the complex featuring a pincer coordination mode renders a hemilabile coordination to the ruthenium center through C=O group of the amide function along with a protic *NH* moiety adjacent to the coordinating oxygen atom. In addition the pincer type NHC complex exhibits good catalytic performances towards oxidation of alcohols. Activated alcohols were almost quantitatively converted into the corresponding aldehydes, whereas the deactivated alcohols were converted into the aldehydes with moderate to poor yield. In this work, we have also made substantial improvement in the catalytic results by improving yields within shorter reaction times and also avoided the usage of halogenated solvents in the catalytic transformations.

EXPERIMENTAL

General Synthetic methods, materials and physical measurements:

Solvents and reagents were purchased from *Sigma Aldrich* or *Acros Organics* in analytical grade and used without further purification. NMR spectra were recorded on a *Bruker AVANCE DPX-400* spectrometer (1H, 400.13 MHz; 13C, 100.61 MHz) with tetramethylsilane as an internal standard. Elemental microanalyses were performed at the *Taiwan Instrumentation Center*. IR spectra were recorded on a *Mattson Genesis Series FT- spectrophotometer*. G.C analyses were performed with a *GC9800* gas chromatography (*Shanghai Kechuang Chromatograph Instrument Co.*) equipped with a flame ionization detector and a 10m (2.65 μm film thickness) *RESTEK Rtx-2887* fused silica capillary column. 2-imidazol-1-ylmethyl-pyridine,[33a] 2-bromo-*N*,*N*-diphenyl-acetamide, and 2-bromo-*N*-phenyl-acetamide[35] were prepared according to literature protocols.

Synthesis

1-(diphenylcarbamoyl-methyl)-3-pyridylmethyl-imidazolium bromide (1a)

A mixture of 2-imidazol-1-ylmethyl-pyridine (0.522 g, 3.28 mmol) and 2-bromo-*N*,*N*-diphenyl-acetamide (0.960 g, 3.28 mmol) in CH_3CN (20 mL) was heated under reflux for 6 h. The reaction mixture was cooled and poured into diethyl ether (100 mL) and the resulting yellow precipitate was filtered. The yellow solid was recrystallized three time by dissolving with methanol (10 mL) and titurated with diethyl ether (100 mL) to obtain white product **1a** (1.265 g, 86 % yield). ^{1}H NMR ($CDCl_3$): δ 9.89 (s, 1H), 8.36 (dd, J_{H-H} = 4.6, 1.7 Hz, 1H), 7.77 (s, 1H), 7.71 (d, J_{H-H} = 7.8 Hz, 2H), 7.53 (td, J_{H-H} = 7.7, 1.8 Hz, 1H), 7.40 (q, J_{H-H} = 7.8 Hz, 3H), 7.31 (t, J_{H-H} = 7.7, 3H), 7.27 (s, 1H), 7.12 (t, J_{H-H} = 7.5 Hz, 3H), 7.04 (d, J_{H-H} = 7.5 Hz, 1H), 5.32 (s, 2H), 5.23 (s, 2H) ppm. ^{13}C NMR (CD_3CN): δ 165.1 (*C*=O), 153.2 (N*C*N), 149.7, 142.6, 140.5, 137.9, 137.6, 130.2, 129.5, 129.1, 126.8, 124.3, 123.8, 123.0, 122.1, 53.5, 51.9 ppm. IR (KBr): ν_{max} (cm^{-1}) 1681 (C=O). Mass (MALDI): *m*/*z* 368 for [M^+]

1-phenylcarbamoylmethyl-3-pyridylmethyl-3H-imidazolium bromide (1b)

A mixture of 2-Imidazol-1-ylmethyl-pyridine (0.340 g, 2.14 mmol) and 2-bromo-*N*-phenyl-acetamide (0.456 g, 2.14 mmol) in CH_3CN (20 mL) was heated under reflux for 6 h. Following the procedure similar to that of **1a**, product **1b** was obtained as brown solid (0.717 g, 90 % yield). ^{1}H NMR ($CDCl_3$): δ 10.65 (s, 1H), 9.71 (s, 1H), 8.43 (d, J_{H-H} = 4.5 Hz, 1H), 7.60 (m, 4H), 7.48 (t, J_{H-H} = 8.0 Hz, 2H), 7.14 (m, 3H), 6.95 (t, J_{H-H} = 7.5 Hz, 1H), 5.53 (s, 2H), 5.50 (s, 2H) ppm. ^{13}C NMR (CD_3CN): δ 163.0 (*C*=O), 152.1 (N*C*N), 149.9, 137.7, 137.6, 137.3, 128.8, 124.5, 124.0, 123.6, 123.5, 122.2, 120.1, 54.1, 52.3 ppm. IR (KBr): ν_{max} (cm^{-1}) 1693 (C=O); 3399 (N–H stretching). Mass (MALDI): *m*/*z* 293 for [M^+].

[2a]

Ag_2O (0.421 g, 1.81 mmol) was added into a CH_2Cl_2 (10 mL) solution of **1a** (0.540 g, 1.25 mmol) and the resultant suspension was stirred at ambient temperature for 4 h under exclusion of light. After this time, the reaction mixture was filtered through Celite and the filtrate was dried *in vacuo*. The residue was dissolved in CH_2Cl_2 (5 mL) and the solution was added into diether ether (30 mL) to yield yellow precipitate. Upon filtration and drying *in vacu*o, [**2a**] was obtained as yellow solid (0.332 g, 31.4% yield). ^{1}H NMR ($CDCl_3$): δ 8.54 (d, J_{H-H} = 5.1 Hz , 2H), 7.66 (t, J_{H-H} = 7.8 Hz, 2H), 7.43 (m, 12H), 7.28 (m, 6H), 7.22–7.15 (m, 10H), 5.35 (s, 4H), 4.87 (s, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 182.9 (N*C*N), 170.1 (*C*=O), 166.2, 155.8, 155.2, 149.7, 141.7, 140.5, 137.5, 130.7, 129.1, 126.7, 126.0, 123.9, 123.4, 123.2, 123.0, 122.7, 122.2, 121.8, 120.4, 57.0 (*C*H_2), 53.9 (*C*H_2) ppm. IR (KBr): ν_{max} (cm^{-1}) 1687 (C=O). Mass (MALDI): *m*/*z* 846.4 for [M^+]. *Anal. Calcd.* for $C_{46}H_{40}N_8O_2AgBr$: C, 59.76; H, 4.36; N, 12.12. Found: C, 59.58; H, 4.22; N, 11.98.

[2b]

To a solution of **1b** (0.232 g, 0.621 mmol) in dichloromethane (5 mL) and methanol (0.5 mL) was added Ag_2O (0.220 g, 0.948 mmol) and the suspension was stirred at ambient temperature for 4 h under exclusion of light. The reaction mixture was filtered through Celite followed by drying the filtrate *in vacuo*. A solution of the resultant residue in dichloromethane (5 mL) was poured into diethylether (30 mL) to yield an yellow precipitate, which was separated and further dried *in vacuo* to obtain **2b** as yellow solid (0.124 g, 26.6 % yield). ^{1}H NMR ($CDCl_3$): δ 8.48 (d, J_{H-H} = 4.8 Hz, 2H), 7.71 (d, J_{H-H} = 8.0 Hz, 4H), 7.56 (t, J_{H-H} = 8.1 Hz, 2H), 7.20 (m, 8H), 7.04 (m, 8H), 5.28 (s, 8H) ppm. ^{13}C NMR ($CDCl_3$): δ 182.1 (N*C*N), 165.4 (*C*=O), 155.1, 149.6, 139.0, 138.6, 137.3, 128.6, 123.9, 123.5, 123.2, 122.2, 121.2, 120.5, 120.0, 56.8, 54.6 ppm. IR (KBr): ν_{max} (cm^{-1}) 1693 (C=O), 3262 (N–H stretching). Mass (MALDI): *m*/*z* 693 [M^+]. *Anal. Calcd.* for $C_{34}H_{32}N_8O_2AgBr$: C, 52.86; H, 4.18; N, 14.51. Found: C, 52.65; H, 4.06; N, 14.32.

[3a]

$[Ru(PPh_3)_3Cl_2]$ (1.43 g, 1.5 mmol) was added into a solution of [**2a**] (0.70 g , 0.75 mmol) in CH_3CN (5 mL) and the mixture was heated under reflux for 5 h, filtration of the reaction mixture yielded a clear solution. Solvent was removed *in vacuo* and the residue was suspended in a mixture of CH_2Cl_2 (50 mL) and H_2O (35 mL) and the product was extracted (×3 times) from the aqueous phase. The aqueous extracts were collected and dried *in vacuo* to obtain [**3a**] (0.536 g, 80.7% yield). ^{1}H NMR ($CDCl_3$): δ 9.58 (d, J_{H-H} = 4.0 Hz, 1H), 7.83 (m, 5H), 7.36 (m, 6H), 7.19 (m, 6H), 7.09 (m, 3H), 7.02 (m, 6H), 6.86 (m, 3H), 6.49 (s, 1H), 6.11 (d, J_{H-H} = 16.0 Hz, 1H), 5.94 (d, J_{H-H} = 16.0 Hz, 1H), 4.30 (d, J_{H-H} = 17.0 Hz, 1H), 2.49 (d, J_{H-H} = 17.4 Hz, 1H), 2.01 (s, 3H), 1.78 (s, 3H), 1.63 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$): δ 180.6 (N*C*N), 167.0 (*C*=O), 156.6, 154.4, 141.3, 139.6, 138.1, 130.6, 129.0, 128.8, 128.7, 128.6, 128.0, 127.9, 127.5, 126.5, 126.2, 125.6, 124.9, 124.7, 124.2, 124.0,

121.3, 55.5, 52.4, 4.7, 4.0 ppm. ^{31}P NMR (300MHz, $CDCl_3$): δ 47.25 ppm. IR (KBr): ν_{max} (cm^{-1}) 1675 (C=O). Mass (MALDI): *m/z* 885 for $[M - CH_3CN + 2Cl]^+$ and 767 for $[M - 3{\cdot}CH_3CN + Cl]^+$. *Anal. Calcd.* for $C_{47}H_{44}Cl_2N_7OPRu$: C, 60.97; H, 4.79; N, 10.59. Found: C, 60.71; H, 4.86; N, 10.50.

[4a]

An aqueous solution (H_2O, 5 mL) of [**3a**] (0.329 g, 0.355 mmol) and NH_4PF_6 (0.12 g, 0.75 mmol) was stirred at ambient temperature for 24 h, after which the reaction mixture was extracted in CH_2Cl_2 (10 mL × 3) and the solvent was removed *in vacuo*. The resultant residue was further washed with minimal amounts of $CHCl_3$ (1 mL × 3) and dried *in vacuo* to obtain [**4a**] as green solid (0.395 g, 96.7% yield). ^{1}H NMR (CD_3CN): δ 9.01 (d, J_{H-H} = 5.7 Hz, 1H), 8.09 (t, J_{H-H} = 15.1 Hz, 1H), 7.75 (d, J_{H-H} = 7.7 Hz, 1H), 7.63 (t, J_{H-H} = 6.8 Hz, 2H), 7.56 (m, 4H), 7.36 (m, 12H), 7.22 (d, J_{H-H} = 7.4 Hz, 1H), 7.16 (d, J_{H-H} = 7.8 Hz, 2H), 7.09 (m, 2H), 7.02 (d, J_{H-H} = 7.6 Hz, 2H), 6.91 (d, J_{H-H} = 2.2 Hz, 1H), 5.71 (d, J_{H-H} = 16.6 Hz, 1H), 5.43 (d, J_{H-H} = 16.6 Hz, 1H), 4.07 (d, J_{H-H} = 16.5 Hz, 1H), 2.94 (d, J_{H-H} = 16.8 Hz, 1H), 2.16 (s, 3H), 1.99 (s, 3H), 1.72 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$): δ 179.5 (N*C*N), 167.4 (*C*=O), 157.0, 155.5, 142.9, 141.2, 140.4, 134.7, 131.6, 131.3, 130.1, 129.8, 129.6, 129.5, 128.5, 127.8, 127.0, 126.8, 126.6, 124.6, 123.6, 122.9, 55.6, 32.1, 4.9, 4.5 ppm. ^{31}P NMR (CD_3COCD_3): δ 45.0 ppm. IR (KBr): ν_{max} (cm^{-1}) 1683 (C=O). Mass (MALDI): *m/z* 920 for $[M + PF_6 - 2{\cdot}CH_3CN]^+$), 733 for $[M - 3{\cdot}CH_3CN]^+$. *Anal. Calcd.* for $C_{47}H_{44}F_{12}N_7OP_3Ru$: C, 49.26; H, 3.87; N, 8.56. Found: C, 49.44; H, 3.93; N, 8.51.

[3b]

A similar procedure as described for [**4a**], starting from $[Ru(PPh_3)_3Cl_2]$ (1.280 g, 1.30 mmol) and [**2b**] (0.505 g , 0.653 mmol) was followed to obtain [**3b**]. An exception being, the chloride salt of [**3b**] could not be isolated directly from the aqueous reaction mixture, hence the aqueous solution was further treated with NH_4PF_6 (0.212 g, 1.31 mmol). Other work-up steps, analogous to that in the preparation of [**4a**] was followed to obtain [**3b**] as yellow solid (0.177 g, 26.3% yield). ^{1}H NMR (CD_3CN): δ 9.34 (s, 1H), 9.13 (d, J_{H-H} = 3.0 Hz, 1H), 8.01 (t, J_{H-H} = 7.8 Hz, 1H), 7.73 (d, J_{H-H} = 7.7 Hz, 1H), 7.61 (s, 1H), 7.55–7.32 (m, 20H), 7.21 (t, J_{H-H} = 11.0 Hz ,1H), 6.95 (s, 1H), 5.72 (d, J_{H-H} = 16.1 Hz, 1H), 5.49–5.42 (m, 1H), 4.30 (d, J_{H-H} = 16.7 Hz, 1H), 3.74 (d, J_{H-H} = 16.7 Hz, 1H), 1.99 (s,3H), 1.92 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$): δ 188.5 (N*C*N), 171.5 (C=O), 157.8, 155.9, 130.1, 136.7, 134.5, 133.3, 132.9, 132.0, 130.4, 130.0, 129.6, 129.6, 127.6, 127.0, 125.9, 124.6, 124.4, 123.5, 121.5, 120.6, 56.2, 52.9, 3.9 ppm. ^{31}P NMR (CD_3CN): δ 48.21 ppm. IR (KBr): ν_{max} (cm^{-1}) 1621 (C=O), 3396 (N–H stretching). Mass (MALDI): *m/z* 1027 for $[M + 2{\cdot}PF_6]^+$ and 841 for $[M + PF_6 - CH_3CN]^+$. *Anal. Calcd.* for $C_{39}H_{37}F_{12}N_6OP_3Ru{\cdot}CH_2Cl_2$: C, 43.14; H, 3.53; N, 7.55. Found: C, 43.27; H, 3.57; N, 7.51.

General procedure for the catalytical oxidation of alcohols.

In a standard catalytic experiment, the alcohol substrate (2.0 mmol), ruthenium–NHC pre-catalyst (5.0 mol%), KO^{t}Bu (1.0 mmol), and toluene (5 mL) were charged into a screw capped *vial* under air and heated at 100 ^{o}C in an oil bath. After the completion of the catalytic reaction, the reaction mixture was extracted in diethyl ether/water system (1:1, *V*:*V*). The organic phase was separated and ether was removed *in vacuo*. The isolated product yields were monitored by NMR spectroscopy.

X-ray crystallography.

The single crystals suitable for X-ray diffraction analyses were obtained by slow diffusion of diethyl ether into a CH_3CN solution of **4a** or by slow evaporation of CH_2Cl_2 solution of **3b**. Data was collected on an APEX II diffractometer, using graphite monochromatic Mo Kα radiation (λ = 0.71073 Å). Data reduction was performed with SAINT, which corrects for Lorentz and polarization effects. Absorption corrections were performed using multiscan (SADABS).[36] All H atoms were added in idealized positions. Structures were solved by the use of direct methods and refinement was performed by the least-squares methods on F^2 with the SHELXL-97 package.[37] Crystal data, including the details of data collection, refinement and complete geometric information are available in CIF format.

Acknowledgements

The authors acknowledge the National Science Council (Taiwan) and National Dong Hwa University for the financial support.

Notes and references

Department of Chemistry, National Dong Hwa University, Hualien 974, Taiwan, ROC. *Fax:+886-3-8633570; Tel: +886-3-8633577; E-mail: hws@mail.ndhu.edu.tw*.

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: Crystal data and refinement parameters are listed in Table S1 and Crystal data, including the details of data collection, refinement and complete geometric information are available in CIF format. CCDC indexing numbers: 941843 for **3b** and 941842 for **4a**. See DOI: 10.1039/b000000x/

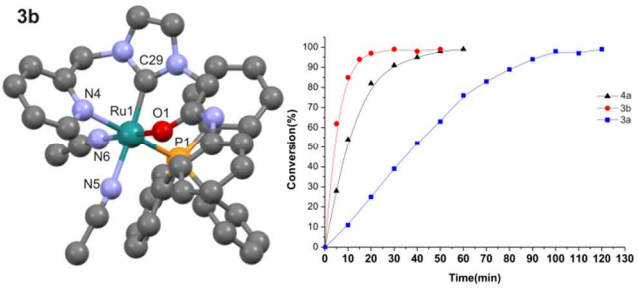
References:

1. (a) S. Diez-Gonzalez, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612-3676; (b) S. Díez-González and S. P. Nolan, *Coord. Chem. Rev.*, 2007, **251**, 874–883; (c) F. E. Hahn and M. C. Jahnke, *Angew. Chem. Int. Ed.*, 2008, **47**, 3122-3172; (d) R. H. Crabtree, *Coord. Chem. Rev.*, 2007, **251**, 595; (e) H. Jacobsen, A. Correa, A. Poater, C. Costabile and L. Cavallo, *Coord. Chem. Rev.*, 2009, **253**, 687-703; (f) J. C. Lin, R. T. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. Lin, *Chem. Rev.*, 2009, **109**, 3561-3598.

2. (a) E. A. B. Kantchev, C. J. O'Brien and M. G. Organ, *Angew. Chem. Int. Ed.*, 2007, **46**, 2768-2813; (b) B. Yiğit, M. Yiğit, İ. Özdemir and E. Çetinkaya, *Transition Met. Chem.*, 2012, **37**, 297–302.
3. (a) F. E. Hahn, *Chemcatchem*, 2013, **5**, 419-430; (b) F. E. Hahn, A. R. Naziruddin, A. Hepp and T. Pape, *Organometallics*, 2010, **29**, 5283–5288; (c) A. R. Naziruddin, A. Hepp, T. Pape and F. E. Hahn, *Organometallics*, 2011, **30**, 5859-5866; (d) T. Kosterke, T. Pape and F. E. Hahn, *J. Am. Chem. Soc.*, 2011, **133**, 2112-2115; (e) N. Meier, F. E. Hahn, T. Pape, C. Siering and S. R. Waldvogel, *Eur. J. Inorg. Chem.*, 2007, 1210-1214.
4. (a) C. S. Lee, S. Sabiah, J. C. Wang, W. S. Hwang and I. J. B. Lin, *Organometallics*, 2010, **29**, 286-289; (b) C. S. Lee, R. R. Zhuang, S. Sabiah, J. C. Wang, W. S. Hwang and I. J. B. Lin, *Organometallics*, 2011, **30**, 3897-3900; (c) K. Li, X. Guan, C. W. Ma, W. Lu, Y. Chen and C. M. Che, *Chem Commun.*, 2011, **47**, 9075-9077; (d) K. Li, G. Cheng, C. S. Ma, X. G. Guan, W. M. Kwok, Y. Chen, W. Lu and C. M. Che, *Chem. Sci.*, 2013, **4**, 2630-2644.
5. (a) L. Kaps, B. Biersack, H. Muller-Bunz, K. Mahal, J. Munzner, M. Tacke, T. Mueller and R. Schobert, *J. Inorg. Biochem.*, 2012, **106**, 52-58; (b) R. Wai-Yin Sun, A. Lok-Fung Chow, X.-H. Li, J. J. Yan, S. Sin-Yin Chui and C.-M. Che, *Chem. Sci.*, 2011, **2**, 728; (c) F. Hackenberg, H. Müller-Bunz, R. Smith, W. Streciwilk, X. Zhu and M. Tacke, *Organometallics*, 2013, **32**, 5551-5560; (d) T. Zou, C. T. Lum, S. S. Chui and C. M. Che, *Angew. Chem. Int. Ed.*, 2013, **52**, 2930-2933.
6. N. Tsoureas, A. A. Danopoulos, A. A. D. Tulloch and M. E. Light, *Organometallics*, 2003, **22**, 4750-4758.
7. (a) F. E. Hahn, M. C. Jahnke and T. Pape, *Organometallics*, 2006, **25**, 5927-5936; (b) H. Salem, M. Schmitt, U. Herrlich, E. Kuhnel, M. Brill, P. Nagele, A. L. Bogado, F. Rominger and P. Hofmann, *Organometallics*, 2013, **32**, 29-46; (c) O. Kaufhold, A. Stasch, P. G. Edwards and F. E. Hahn, *Chem. Commun.*, 2007, 1822-1824; (d) E. M. Schuster, M. Botoshansky and M. Gandelman, *Dalton Trans*, 2011, **40**, 8764-8767.
8. (a) K. M. Lee, J. C. C. Chen and I. J. B. Lin, *J. Organomet. Chem.*, 2001, **617**, 364-375; (b) Y. Zhou, Z. Xi, W. Chen and D. Wang, *Organometallics*, 2008, **27**, 5911-5920; (c) V. J. Catalano and A. L. Moore, *Inorg. Chem.*, 2005, **44**, 6558-6566; (d) E. Kluser, A. Neels and M. Albrecht, *Chem Commun.*, 2006, 4495-4497; (e) X. Wang, S. Liu, L.-H. Weng and G.-X. Jin, *Organometallics*, 2006, **25**, 3565-3569; (f) Y. Cheng, J. F. Sun, H. L. Yang, H. J. Xu, Y. Z. Li, X. T. Chen and Z. L. Xue, *Organometallics*, 2009, **28**, 819-823; (g) X. W. Li, G. F. Wang, F. Chen, Y. Z. Li, X. T. Chen and Z. L. Xue, *Inorg. Chim. Acta*, 2011, **378**, 280-287; (h) N. Gurbuz, E. O. Ozcan, I. Ozdemir, B. Cetinkaya, O. Sahin and O. Buyukgungor, *Dalton Trans*, 2012, **41**, 2330–2339; (i) F. E. Fernández, M. C. Puerta and P. Valerga, *Organometallics*, 2011, **30**, 5793–5802; (j) H. Ohara, W. N. O. Wylie, A. J. Lough and R. H. Morris, *Dalton Trans*, 2012, **41**, 8797–8808; (k) W. B. Cross, C. G. Daly, Y. Boutadla and K. Singh, *Dalton Trans*, 2011, **40**, 9722–9730; (l) F. E. Fernández, M. C. Puerta and P. Valerga, *Organometallics*, 2012, **31**, 6868–6879.
9. C. S. Lee, R. R. Zhuang, J. C. Wang, W. S. Hwang and I. J. B. Lin, *Organometallics*, 2012, **31**, 4980-4987.
10. B. Liu, Q. Xia and W. Chen, *Angew. Chem. Int. Ed.*, 2009, **48**, 5513-5516.
11. (a) H. M. Peng, G. Song, Y. Li and X. Li, *Inorg. Chem.*, 2008, **47**, 8031-8043; (b) H. M. Peng, R. D. Webster and X. W. Li, *Organometallics*, 2008, **27**, 4484-4493.
12. (a) S. B. Fuwei Li, and T. S. Andy Hor, *Organometallics* 2008, **27**, 672-677; (b) F. Li, J. J. Hu, L. L. Koh and T. S. Hor, *Dalton Trans*, 2010, **39**, 5231-5241.
13. (a) W. A. Herrmann, L. J. Goossen and M. Spiegler, *Organometallics*, 1998, **17**, 2162-2168; (b) V. César, S. Bellemin-Laponnaz and L. H. Gade, *Organometallics*, 2002, **21**, 5204-5208; (c) M. C. Perry, X. Cui, M. T. Powell, D. R. Hou, J. H. Reibenspies and K. Burgess, *J. Am. Chem. Soc.*, 2003, **125**, 113-123; (d) N. Schneider, V. Cesar, S. Bellemin-Laponnaz and L. H. Gade, *Organometallics*, 2005, **24**, 4886-4888; (e) S. Nanchen and A. Pfaltz, *Chem.–Eur. J.*, 2006, **12**, 4550-4558; (f) J. Zhao and K. Burgess, *Org Lett*, 2009, **11**, 2053-2056.
14. S. Gu and W. Chen, *Organometallics*, 2009, **28**, 909-914.
15. (a) S. Burling, B. M. Paine, D. Nama, V. S. Brown, M. F. Mahon, T. J. Prior, P. S. Pregosin, M. K. Whittlesey and J. M. Williams, *J. Am. Chem. Soc.*, 2007, **129**, 1987-1995; (b) S. Burling, M. F. Mahon, R. E. Powell, M. K. Whittlesey and J. M. J. Williams, *J. Am. Chem. Soc.*, 2006, **128**, 13702-13703; (c) A. E. Ledger, M. F. Mahon, M. K. Whittlesey and J. M. Williams, *Dalton Trans*, 2009, **0**, 6941-6947.
16. J. I. van der Vlugt, *Eur. J. Inorg. Chem.*, **2012**, 363-375.
17. D. Yuan, H. Tang, L. Xiao and H. V. Huynh, *Dalton Trans*, 2011, **40**, 8788-8795.
18. P. Elena, G. Mark, J. W. S. Linda, R. Haim, B.-D. Yehoshoa and M. David, *Chem.–Eur. J.*, 2004, **10**, 4673-4684.
19. (a) M. S. Rosen, C. L. Stern and C. A. Mirkin, *Chem. Sci.*, 2013, **4**, 4193; (b) J. I. van der Vlugt, *Eur. J. Inorg. Chem.*, 2012, 363-375.
20. (a) M. K. Samantaray, V. Katiyar, D. Roy, K. L. Pang, H. Nanavati, R. Stephen, R. B. Sunoj and P. Ghosh, *Eur. J. Inorg. Chem.*, 2006, 2975-2984; (b) M. K. Samantaray, K. Pang, M. M. Shaikh and P. Ghosh, *Inorg. Chem.*, 2008, **47**, 4153-4165.
21. C. Gandolfi, M. Heckenroth, A. Neels, G. Laurenczy and M. Albrecht, *Organometallics*, 2009, **28**, 5112-5121.
22. M. V. Jiménez, J. Fernández-Tornos, J. J. Pérez-Torrente, F. J. Modrego, S. Winterle, C. Cunchillos, F. J. Lahoz and L. A. Oro, *Organometallics*, 2011, **30**, 5493-5508.
23. (a) R. A. Sheldon and I. W. C. E. Arends, in *Transition Metals for Organic Synthesis*, Wiley-VCH Verlag GmbH, 2008, pp. 200-213; (b) M. Pagliaro, S. Campestrini and R. Ciriminna, *Chem. Soc. Rev.*, 2005, **34**, 837-845; (c) S.-I. Murahashi and N. Komiya, in *Modern Oxidation Methods*, Wiley-VCH Verlag GmbH & Co. KGaA, 2005, pp. 165-191.
24. (a) R. A. Sheldon and J. K. Kochi, in *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981, pp. 350-382; (b) F. A. Luzzio and F. S. Guziec, Jr., *Org. Prep. Proced. Int.*, 1988, **20**, 533; (c) T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037-3058; (d) R. J. Taylor, M. Reid, J. Foot and S. A. Raw, *Acc. Chem. Res.*, 2005, **38**, 851-869; (e) T. T. Tidwell, *Synthesis*, 1990, **1990**, 857-870; (f) J. Ni, W. J. Yu, L. He, H. Sun, Y. Cao, H. Y. He and K. N. Fan, *Green Chem.*, 2009, **11**, 756-759; (g) M. Uyanik and K. Ishihara, *Chem Commun.*, 2009, 2086-2099; (h) H. Tomioka, K. Takai, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, 1981, **22**, 1605-1608; (i) A. M. Maione and A. Romeo, *Synthesis*, 1984, **1984**, 955-957.

25. M. Shibuya, Y. Osada, Y. Sasano, M. Tomizawa and Y. Iwabuchi, *J. Am. Chem. Soc.*, 2011, **133**, 6497-6500.
26. (a) D. R. Jensen, J. S. Pugsley and M. S. Sigman, *J. Am. Chem. Soc.*, 2001, **123**, 7475-7476; (b) E. M. Ferreira and B. M. Stoltz, *J. Am. Chem. Soc.*, 2001, **123**, 7725-7726; (c) M. J. Schultz, C. C. Park and M. S. Sigman, *Chem. Commun.*, 2002, 3034-3035; (d) S. K. Mandal, D. R. Jensen, J. S. Pugsley and M. S. Sigman, *J. Org. Chem.*, 2003, **68**, 4600-4603; (e) B. Z. Zhan and A. Thompson, *Tetrahedron*, 2004, **60**, 2917-2935; (f) S. Mannam, S. K. Alamsetti and G. Sekar, *Adv. Synth. Catal.*, 2007, **349**, 2253-2258; (g) H. Mizoguchi, T. Uchida, K. Ishida and T. Katsuki, *Tetrahedron Lett.*, 2009, **50**, 3432-3435; (h) R. Dileep and B. R. Bhat, *Appl. Organomet. Chem.*, 2010, **24**, 663-666; (i) C. Y. Han, M. Yu, W. J. Sun and X. Q. Yao, *Synlett*, 2011, **2011**, 2363-2368; (j) T. Kunisu, T. Oguma and T. Katsuki, *J. Am. Chem. Soc.*, 2011, **133**, 12937-12939; (k) J. M. Hoover and S. S. Stahl, *J. Am. Chem. Soc.*, 2011, **133**, 16901-16910; (l) T. Nishii, T. Ouchi, A. Matsuda, Y. Matsubara, Y. Haraguchi, T. Kawano, H. Kaku, M. Horikawa and T. Tsunoda, *Tetrahedron Lett.*, 2012, **53**, 5880-5882; (m) S. S. Shen, V. Kartika, Y. S. Tan, R. D. Webster and K. Narasaka, *Tetrahedron Lett.*, 2012, **53**, 986-990.
27. (a) R. Sheldon, *Green Chemistry*, 2000, **2**, G1-G4; (b) P. T. Anastas, L. B. Bartlett, M. M. Kirchhoff and T. C. Williamson, *Catal. Today*, 2000, **55**, 11-22; (c) R. A. Sheldon and H. van Bekkum, in *Fine Chemicals through Heterogeneous Catalysis*, Wiley-VCH Verlag GmbH, 2007, pp. 473-551; (d) T. Matsumoto, M. Ueno, N. Wang and S. Kobayashi, *Chem.–Asian J.*, 2008, **3**, 196-214; (e) N. Mizuno and K. Yamaguchi, *Catal. Today*, 2008, **132**, 18-26.
28. (a) J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg and D. Milstein, *Organometallics*, 2004, **23**, 4026-4033; (b) Y. Zhu, B. Zhao and Y. Shi, *Org Lett*, 2013, **15**, 992-995.
29. (a) T. Naota, H. Takaya and S. I. Murahashi, *Chem. Rev.*, 1998, **98**, 2599-2660; (b) A. Dijksman, A. Marino-González, A. Mairata i Payeras, I. W. C. E. Arends and R. A. Sheldon, *J. Am. Chem. Soc.*, 2001, **123**, 6826-6833.
30. (a) G. Rivera and R. H. Crabtree, *J Mol Catal a-Chem*, 2004, **222**, 59-73; (b) C. Y. Liao, K. T. Chan, J. Y. Zeng, C. H. Hu, C. Y. Tu and H. M. Lee, *Organometallics*, 2007, **26**, 1692-1702.
31. P. Marcé, C. Godard, M. Feliz, X. Yáñez, C. Bo and S. Castillón, *Organometallics*, 2009, **28**, 2976-2985.
32. (a) W. P. Fehlhammer, T. Bliss, U. Kernbach and I. Brüdgam, *J. Organomet. Chem.*, 1995, **490**, 149-153; (b) W. A. Herrmann, J. Schwarz, M. G. Gardiner and M. Spiegler, *J. Organomet. Chem.*, 1999, **575**, 80-86; (c) A. A. Danopoulos, A. A. D. Tulloch, S. Winston, G. Eastham and M. B. Hursthouse, *Dalton Trans*, 2003, 1009-1015; (d) M. Heckenroth, A. Neels, H. Stoeckli-Evans and M. Albrecht, *Inorg. Chim. Acta*, 2006, **359**, 1929-1938; (e) M. C. Jahnke, T. Pape and F. E. Hahn, *Z. Naturforsch. B*, 2010, **65**, 341-346; (f) D. Serra, P. Cao, J. Cabrera, R. Padilla, F. Rominger and M. Limbach, *Organometallics*, 2011, **30**, 1885-1895; (g) P. Cao, J. Cabrera, R. Padilla, D. Serra, F. Rominger and M. Limbach, *Organometallics*, 2012, **31**, 921-929; (h) A. Raba, M. Cokoja, S. Ewald, K. Riener, E. Herdtweck, A. Pöthig, W. A. Herrmann and F. E. Kühn, *Organometallics*, 2012, **31**, 2793-2800.
33. (a) J. A. Love, M. S. Sanford, M. W. Day and R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, **125**, 10103-10109; (b) W.-Z. Zhang, R. He and R. Zhang, *Eur. J. Inorg. Chem.*, 2007, 5345-5352; (c) J. Maurer, M. Linseis, B. Sarkar, B. Schwederski, M. Niemeyer, W. Kaim, S. Zalis, C. Anson, M. Zabel and R. F. Winter, *J. Am. Chem. Soc.*, 2008, **130**, 259-268; (d) M. Martín, H. Horváth, E. Sola, A. g. Kathó and F. Joó, *Organometallics*, 2009, **28**, 561-566; (e) Y. B. Lai, C. S. Lee, W. J. Lin, A. R. Naziruddin and W. S. Hwang, *Polyhedron*, 2013, **53**, 243-248; (f) A. R. Naziruddin, Z. J. Huang, W. C. Lai, W. J. Lin and W. S. Hwang, *Dalton Trans*, 2013, **42**, 13161-13171.
34. X. Liu, Q. Xia, Y. Zhang, C. Chen and W. Chen, *J. Org. Chem,* 2013, **78**, 8531-8536.
35. E. Galardon, M. Giorgi and I. Artaud, *Dalton Trans*, 2007, 1047-1052.
36. in *APEX, SAINT and SADABS. Bruker AXS Inc.*, Madison, WI., USA, 2004.
37. G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112–122.

TOC Graphics



Ruthenium chelates bearing *N^C^O*-donors in bidentate or pincer coordination modes have been prepared. Ruthenium pincer complex catalyses the oxidation of alcohols to corresponding aldehydes with yields as high as 99%.

For the Table of contents entry:

Donor Functionalized Ruthenium *N*-Heterocyclic Carbene Complexes in Alcohol Oxidation Reactions

Ruthenium chelates bearing *N^C^O*-donors in bidentate or pincer coordination modes catalyses the selective oxidation of alcohols to corresponding aldehydes with yields as high as 99%.