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Authors: Ramesh Rengan, Saranya Sundar, and Małecki Jan Grzegorz

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FULL PAPER

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One-pot Catalytic Approach for the Selective Aerobic Synthesis of Imines from Alcohols and Amines using Efficient Arene Diruthenium(II) Catalysts under Mild Condition

Sundar Saranya,[a] Rengan Ramesh*[a] and Jan Grzegorz Małecki[b]

Abstract: A green and efficient catalytic approach for the selective synthesis of imines in open air at room temperature was achieved with the aid of newly synthesized diruthenium(II) complexes [(η^6-*p*-cymene)$_2$Ru$_2$Cl$_2$(μ-L)] comprising of substituted 1,2-diacylhydrazine ligands. All the new complexes have been fully characterized by analytical and spectral techniques. The solid state structure of representative complex was corroborated with the help of single-crystal X-ray diffraction method. Further, diruthenium(II) complexes enable the selective aerobic oxidation of alcohols to aldehydes. The catalytic reaction operates in the presence of green and economic oxidant air with the release of water as the only by-product. A plausible mechanism is proposed for the synthesis of imines, which is believed to proceed via an aldehyde intermediate.

Introduction

Azomethines/Imines are vital class of nitrogen compounds that are considered to be one of the most versatile components in organic synthesis, agricultural chemicals and pharmaceuticals (Figure 1).[1] Especially, imines containing highly reactive azomethine group are recognized as key intermediates in many organic transformations such as asymmetric synthesis, cross-dehydrogenative couplings, multi-component synthesis and cycloadditions.[2] Hence, development of highly efficient and environmentally benign methodology for the synthesis of imines still remains a significant area of research among the synthetic chemists.

Conventional synthetic routes to imines involve simple condensation of aldehydes or ketones with amines via azeotropic distillation or in the presence of dehydrating agent. Several other known methodologies for imination includes Schmidt reaction, Aza-Wittig reaction, Stieglitz rearrangement.[3] Besides, it can also be achieved by self-condensation of amines, reaction of alkynes and amines, coupling of vinyl bromides with amines, reaction of nitroarenes and primary alcohols in the presence of metal catalyst and so on.[4]

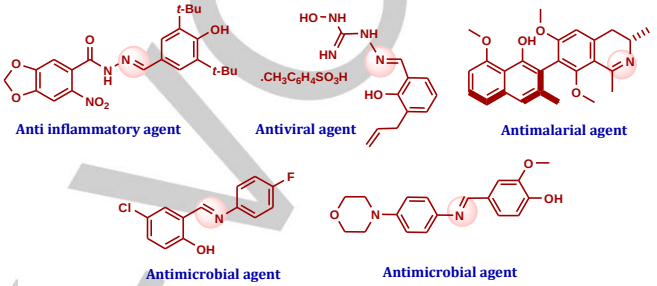

Figure 1. Representative examples for bioactive imines

Although there are several new methodologies reported in the recent years, acceptorless dehydrogenation of alcohols is an efficient and atom-economical alternative, which produces carbonyl compounds, organo-nitrogen compounds such as imines, amines and amides.[5] Further, the reason for this method to be considered worthy is its synthetic applications such as widely available cheaper and less toxic alcohols, non-polluting by-products water or hydrogen gas and oxidant-free synthesis.

The catalytic direct N-alkylation of amines with alcohols by borrowing hydrogen methodology occurs via short-lived imine intermediates which undergo immediate hydrogenation to form the desired amines.[5g] However, selective dehydrogenative imine synthesis was achieved by Milstein's ruthenium PNP-type pincer complex,[5c] where the reaction stops at the imine stage. This breakthrough synthetic methodology attracted the researchers towards the imine chemistry. Several nobel transition metal complexes of Ru, Os and Ir have been reported for imine synthesis, which most often require high temperature, inert atmosphere, special condition and long reaction time.[6] Besides the experimental conditions, few of them suffer from major shortcomings in producing byproducts such as amines/amides/esters. Though there are several pincer type Ru and Os complexes reported for imine synthesis, non-pincer type complexes are not much covered in the literature. Further, alkali metal hydroxides catalysed imine synthesis has also been reported, but the reaction proceeds only at high temperature.[7]

Here we have focused on nobel transition metal catalysts that operate under mild reaction condition (Scheme 1). Riisager and co-workers employed Au/TiO_2(0.2 mol%) heterogeneous catalyst for the imine synthesis with dangerous pure oxygen as the oxidant under ambient conditions (a).[8a] Later, Qing Xus group successfully used palladium catalyst (1 mol%) for mild one-pot synthesis of imines using air as oxidant with good yields of the products, but the drawback is long reaction time (3 days)

[a] Centre for Organometallic Chemistry
School of Chemistry
Bharathidasan University
Tiruchirappalli 620 024
Tamil Nadu, India
E-mail: ramesh_bdu@yahoo.com
Homepage: http://www.bdu.ac.in/centers/comc/
[b] Department of Crystallography
Institute of Chemistry
University of Silesia
40-006 Katowice, Poland

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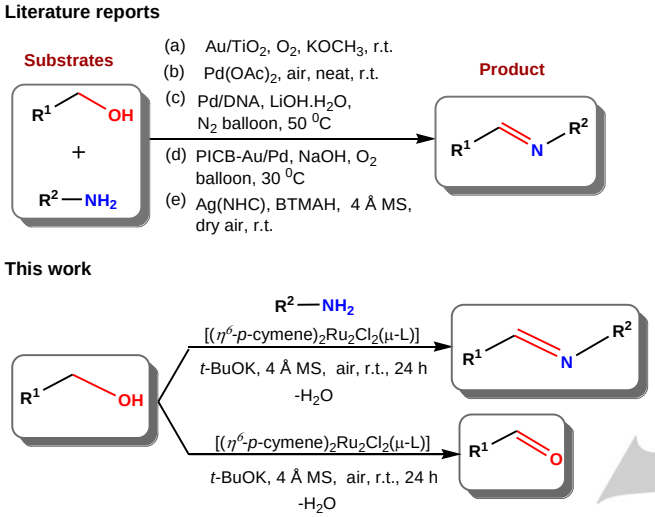
(b).[8b] Wang and co-workers developed Pd/DNA (Pd: 2.9 mol%) catalyst for dehydrogenative imination in H_2O under mild conditions that requires nitrogen atmosphere protection (c).[8c] Kobayashi et al. obtained imines from gold/palladium alloy nanoparticles (1.5 mol%) with molecular oxygen as an oxidant in THF-TFE medium under aerobic condition (d).[8d] One-pot synthesis of imines was achieved using Ag(NHC) (0.1 mol %) catalyst in dry air at room temperature (e). Though the Ag(NHC) catalyst is efficient and versatile, it is not easily accessible from the synthetic point of view. [8e]



Scheme 1. Synthetic strategies of imines

The design of new bimetallic catalysts offers opportunity to modulate the selectivity and activity of the catalytic transformations. The enhanced activities of these catalysts could be achieved by careful crafting of two metal active sites (Figure 2). The increased activity and selectivity of the bimetallic systems are attributed due to the synergic cooperation between the two metals and the bridging ligands. Many of the dinuclear complexes were developed as selective catalysts in organic synthesis. [9a-e]

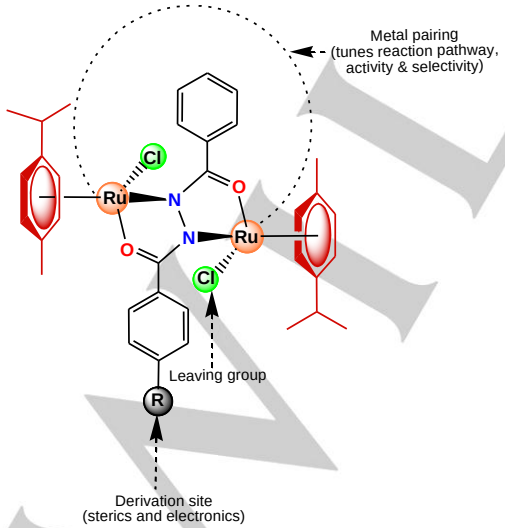
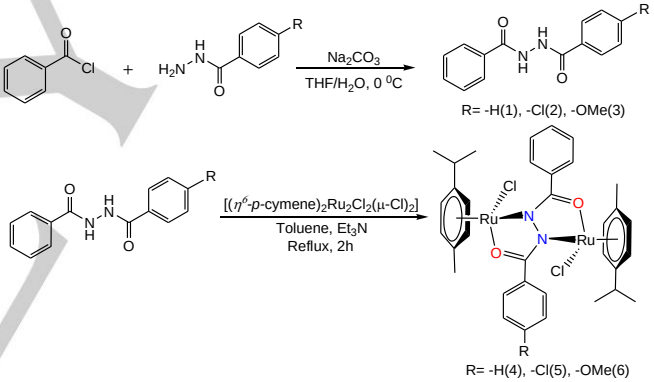


Figure 2. Structure–function relationships in bimetallic system

In continuation of our growing interest on the development of new catalytic systems for various coupling reactions,[10] herein we report arene dinuclear Ru(II) complex for the direct synthesis of imines in the presence of air as greener oxidant under mild condition. To the best of our knowledge, no reports available for the direct synthesis of imines using arene diruthenium(II) catalysts that operate under mild and aerobic condition.

Results and Discussion

Complexes of the type $[(\eta^6\text{-}p\text{-cymene})_2Ru_2Cl_2(\mu\text{-L})]$ were synthesized from the reaction of equimolar mixture of $[(\eta^6\text{-}p\text{-cymene})_2Ru_2Cl_2(\mu\text{-Cl})_2]$ and binucleating ligands, *N*-Benzoylbenzohydrazide (1) or *N*-Benzoyl-4-chlorobenzohydrazide (2) or *N*-Benzoyl-4-methoxybenzohydrazide (3) in toluene for 2 h under reflux condition(Scheme 2). The orange coloured complexes are air-stable and highly soluble in polar organic solvents. All the synthesized complexes were fully characterized with the aid of elemental analysis, IR, UV-Vis, ^{1}H and ^{13}C NMR and Mass spectral techniques. Further, the coordination of the bridging binucleating ligand to two ruthenium metal centers is evidenced by single crystal X-ray method.



Scheme 2. Synthetic route to the arene dinuclear ruthenium(II) complexes.

The Infrared spectra of the ligands (1 - 3) showed characteristic peaks in the region of 3204–2998 cm^{-1}, which are assignable to the two N–H groups.[11] The absence of these N-H bands in the arene dinuclear complexes confirms the coordination of the ligands via hydrazine nitrogen in the ionized form. These ligands also exhibited strong absorptions in the region of 1563–1570 cm^{-1} which correspond to the carbonyl groups, whose frequencies were found to slightly decrease upon complexation. Thus, these observations clearly indicate the coordination of carbonyl oxygen to each ruthenium(II) ion. The IR spectra of the complexes therefore confirm the mode of coordination of the bridging 1,2-benzoylhydrazide ligands to each ruthenium(II) ion via the hydrazine nitrogens and carbonyl oxygens in the ionic and neutral form respectively.

The ^{1}H and ^{13}C NMR spectra of complexes (**4 - 6**) were recorded in $CDCl_3$ and are consistent with the structure proposed. The signals due to NHNH group were observed in the region of δ 10.42 – 10.60 ppm in free uncoordinated ligands, [11]

which disappeared upon the coordination further support that the two ruthenium centers are spanned through the hydrazine nitrogens in the ionized form. The unsymmetrical structural arrangement of complexes **5** and **6** is well supported by the ^{1}H and ^{13}C NMR spectra. The splitting pattern observed for the *p*-cymene protons of complexes **5** and **6** are different from that of complex **4**. This may be attributed due to the substitution at one of the phenyl rings of the ligands, resulting in an unsymmetrical environment of the arene moieties attached to each Ru(II) ion. Similarly, ^{13}C NMR spectra of complexes **4-6** are consistent with the above discussions.

The relative compositions of the complexes have been studied using HR-ESI-MS spectral technique. The positive ESI mass spectra of the complexes **4** – **6** showed peaks corresponding to the cationic fragments $[M - Cl - HCl]^{+}$ at m/z (**4**, 739.1068), (**5**, 745.0551), (**6**, 709.0955) respectively. These results imply that the two chloro (Cl−) groups are labile and possibly replaced under the catalytic reaction condition.

Molecular structure of $[(\eta^{6}\text{-}p\text{-cymene})_2Ru_2Cl_2(\mu\text{-L1})]$ **(4)** has been determined by single-crystal X-ray diffraction analyses. Crystals of **4** grew from slow diffusion of dichloromethane into pet-ether solutions and crystallized in the monoclinic with $P2_1/n$ space group. The molecular structure of the complex **4** is shown in Figure 3, which indicate the formation of the arene dinuclear Ru(II) complexes by the coordination of the bridging ONꓵNO ligand in a monoionised bidentate manner to each ruthenium(II) ion via the hydrazine nitrogen and carbonyl oxygen including one chlorine atom and p-cymene ring. It adopts a piano-stool pseudo octahedral geometry around each Ru(II) ion. In this case, the two *η*6-coordinated arene seats of the piano-stool and chlorine atoms are trans to each other. The bridging chelating ligand binds to each Ru(II) ion via N and O atoms forming two stable five membered chelate rings. The bite angles for O(1)-Ru(1)-N(1), O(1)-Ru(1)-Cl(1) and N(1)-Ru(1)-Cl(1) are 76.40(11)°, 85.02(9)° and 84.04(9)° respectively. The bond lengths for Ru(1)-N(1), Ru(1)-O(1) are 2.087(3)Å and 2.066(2)Å respectively. Further, the Ru···Ru distance in this complex is 4.920(5) Å. The N1−N1^{i} bond distance is 1.427(6) Å, corresponding to N−N single bond. Similarly, the bond length of C1−O1 is 1.280(4) Å, which is consistent with a C=O double bond. Hence, the X-ray crystallographic studies authenticate the structure proposed with the aid of other spectroscopic techniques.

With a new of class of arene dinuclear Ru(II) complexes(**4 - 6**) in hand, we commenced our study by investigating the catalytic activity towards synthesis of imines by the coupling of alcohols and amines. In light of this, 4-methoxy benzyl alcohol (1a) and *p*-anisidine (2a) were taken as benchmark substrates complex **4** (1 mol%) as a model catalyst to optimise the reaction condition. It is known from the literature that there is no set of rules that a particular solvent or a base helps to achieve the greatest efficacy. In order to classify the scope of the catalyst, imination was optimised through the variation of solvents such as toluene, THF, DCM, MeOH in the presence of *t*-BuOK as base at different temperature for 12 h.

To our delight, apolar solvent toluene yielded 90% of the desired imine (Table 1, entry 1). Polar aprotic solvents such as THF and dichloromethane provided yields of 92% and 83% of imines respectively (Table 1, entries 2 and 3). On the other hand methanol furnished 66% of the desired imine, which was

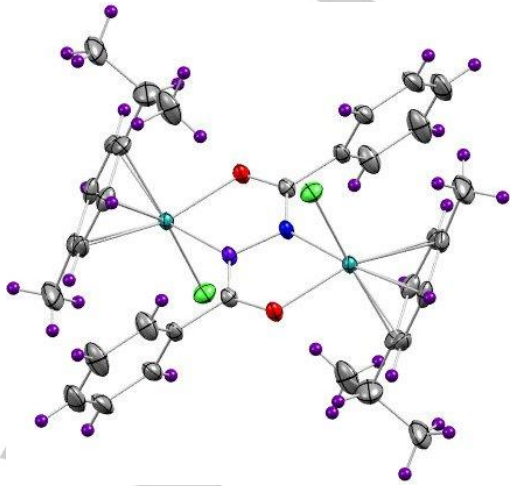


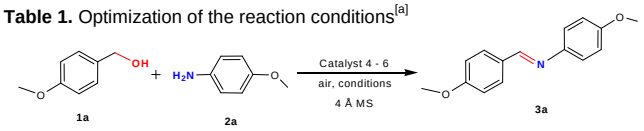
Figure 3. ORTEP plots of complex 4. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ru1−O1 = 2.066 (2), Ru1−N1 = 2.087 (3), Ru1−Cl1 = 2.4121 (10), N1−N1i = 1.427 (6), Ru1−C8 = 2.217 (4), Ru1−C9 = 2.185 (4), Ru1−C10 = 2.165 (4), Ru1− C11 = 2.192 (4), Ru1−C12 = 2.142 (4), Ru1−C13 = 2.186 (4); O1−Ru1− N1= 76.40 (11).

accompanied by considerable amounts of side-products determined by the ^{1}H NMR spectral analysis of the crude (Table 1, entry 4). Hence, THF is a choice of solvent from the optimization. The reaction which showed no reactivity in THF in the absence of base at room temperature, proceeded smoothly under reflux conditions with an appreciable yield of 71% of the corresponding imine (Table 1**,** entries 5 and 6). The reaction did not proceed in the absence of catalyst, both at r.t. and at 66 °C (Table 1**,** entries 7 and 8). Since we were interested in exploring the imination under mild condition, we carried out the base optimisation at room temperature. (Table 1**,** entries 9 – 11). Out of the screened bases, *t*-BuOK was found to be the best choice. Further, the reaction time was extended to 48 h to enhance the product yield, but regrettably no significant improvement was observed (Table 1, entry 12). It is to note that no appreciable yields have been observed when Ru(II) arene and other conventional Ru(II) precursors were used as catalysts.

To further evaluate the catalytic efficiency of complexes **5** and **6**, the model substrates were allowed to react under optimised condition for 24 h at room temperature to yield *N*-(4-methoxybenzylidene)-4-methoxybenzenamine in 63% and 84% respectively (Table 1, entries 13 and 14). Thus we were pleased to find that complex **4** is relatively active among the three complexes. Furthermore, the effect of catalyst loading was also performed. On decreasing the catalyst loading of catalyst **4** from 1 mol% to 0.25 mol%, a substantial drop in the yields of the products were observed (Table 1, entries 15 - 17). Thus, from the data summarised in Table 1, the finest optimum conditions for the diruthenium(II) catalysed imination was achieved by operating the reaction at room temperature under open air with 1 mol % of catalyst **4** in the presence of *t*-BuOK for 24 h.

After arriving at the optimized reaction conditions, we wished to probe the substrate scope and consistency of this methodology. Therefore, we experimented the imine formation by varing the substituents on alcohols and amines in order to examine the breadth of substrates including electron rich and deficient groups tolerated in the reaction (Table 2). In the dehydrogenative imination reaction, *p*-anisidine reacted efficiently with a number of alcohols under the standard

Table 1. Optimization of the reaction conditions[a]

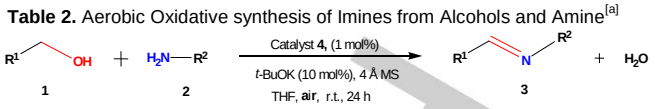


Entry	Complexes	Solvent	Base	T	Yield(%)[d]
1[b]	4 (1 mol%)	Toluene	t-BuOK	70 °C	90
2[b]	4 (1 mol%)	THF	t-BuOK	66 °C	92
3[b]	4 (1 mol%)	DCM	t-BuOK	40 °C	83
4[b]	4(1 mol%`)	MeOH	t-BuOK	65 °C	66
5	4 (1 mol%)	THF	-	r.t.	NR
6	4 (1 mol%)	THF	-	66 °C	71
7	-	THF	t-BuOK	r.t.	NR
8	-	THF	t-BuOK	66 °C	NR
9	4 (1 mol%)	THF	t-BuOK	r.t.	95
10	4 (1 mol%)	THF	KOH	r.t.	91
11	4 (1 mol%)	THF	LiOH.H2O	r.t.	30
12[c]	4 (1 mol%)	THF	t-BuOK	r.t.	95
13	5 (1 mol%)	THF	*t*-BuOK	r.t.	63
14	6 (1 mol%)	THF	*t*-BuOK	r.t.	84
15	4 (0.75 mol%)	THF	*t*-BuOK	r.t.	89
16	4 (0.50 mol%)	THF	*t*-BuOK	r.t.	78
17	4 (0.25 mol%)	THF	*t*-BuOK	r.t.	60

[a] Conditions: 1a (1 mmol), 2a (1 mmol), catalyst (**4 - 6**), 10 mol % of base, 4 Å MS, open air and 5 mL solvent for 24 h. [b] Reaction time was 12 h [c] Reaction time was 48 h. [d] Isolated yields.

conditions (Table 2, entries1-6). The reaction of *p*-anisidine with 4-methoxybenzyl alcohol went smoothly to afford *N*-(4-methoxybenzylidene)-4-methoxybenzenamine (Table 2, entry 1) as the sole product with complete conversion and excellent isolated yield (95%). *para*- and *meta*- substituted methyl benzyl alcohols participated well in the imine formation furnishing good yields with excellent conversions (Table 2, entries 2 and 3). Similarly, the straight forward imination was achieved by the benzyl alcohol bearing electron withdrawing (4-chloro, 3-fluro, 2-bromo) substituents in good isolated yields (Table 2, entries 4, 5 and 6). Further, we extended our investigation by varying the substituents on amines (Table 2, entries 7 - 19). Comparative studies on *para-, meta-, and ortho*- methyl aniline with various benzyl alcohols (4-methyl, benzyl, 4-methoxy) furnished the the corresponding imines in good yields (Table 2, entries 7 - 11). Noteworthy, *ortho*- substituted anilines reacted sluggishly which may be due to the steric hindrance of the methyl group. Coupling of 4-bromoaniline with benzyl alcohol bearing electron donating substituents (4-methyl, 4-methoxy) gave desired imines in moderate yields (Table 2, entries 12, 13). Aniline reacted with benzyl alcohol yielding 81% of *N*-

Table 2. Aerobic Oxidative synthesis of Imines from Alcohols and Amine[a]



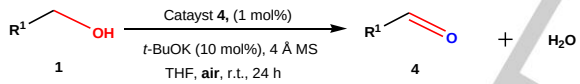
Entry	1	2	3[b]	Conv. %[b]	Yield %[c]
1			:(3a)	>99	95
2			:(3b)	91	86
3			:(3c)	93	91
4			:(3d)	>99	85
5			:(3e)	94	82
6			:(3f)	96	80
7			:(3g)	90	88
8			:(3h)	89	76
9			:(3i)	86	81
10			:(3j)	76	71
11			:(3k)	82	77
12			:(3l)	79	78
13			:(3m)	92	84
14			:(3n)	90	81
15			:(3o)	84	80
16			:(3p)	96	82
17			:(3q)	>99	93
18			:(3r)	80	75
19			:(3s)	79	70
20			:(3t)	30	16
21			:(3u)	-	Trace
22			:(3v)	-	-
23			:(3w)	-	-

[a] Reaction conditions: 1a (1 mmol), 2a (1 mmol), catalyst **4** (1 mol %), t-BuOK (10 mol%), 4 Å molecular seives and THF (5 mL) stirred at r.t. for 24 h in open air.[b] Reactions monitored by GC-MS. [c] Isolated yields.

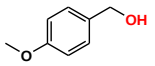
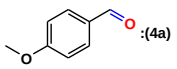
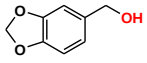
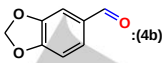
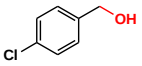
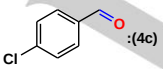
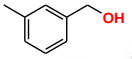
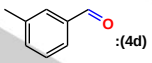
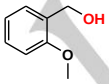
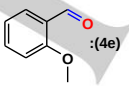
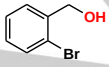
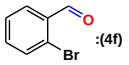
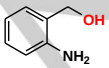
benzylidenebenzenamine(Table 2, entry, 14). On the other hand, The reaction of benzyl amine and benzyl alcohol yielded the corresponding imine in 80% (Table 2, entry, 15). It is gratifying to note that the reaction of thiophen-2-yl-methanol proceeded well to yield the desired imine in good yield. (Table 2, entry 16). Further, piperonyl analogues are considered to be pharmaceutically active.[12] Hence, we wish to explore a range of piperonyl based imines, whose synthesis using this methodology is less covered in the literature. Gratifyingly, we achieved the desired imines with reasonable conversions in good yields (Table 2, entries 17 - 19). To our delight, coupling of piperonyl alcohol with 4-methoxyaniline gave *N*-(benzo[d][1,3]dioxol-5-ylmethylene)-4-methoxybenzenamine in 93% isolated yield with good conversion (Table 2, entry 17). A chiral amine such as (*R*)-(+)-α-methylbenzylamine with 4-methoxybenzyl alcohol gave poor yield of 16% of the corresponding imine under the optimised condition (Table 2, entry 20). We could not succeed in obtaining the expected imines when aromatic secondary alcohols, aliphatic alcohols, and aliphatic amine were used as substrates (Table 2, entries 21 - 23). The isolated imine products were confirmed by ^{1}H and ^{13}C NMR spectral techniques and compared with the literature.

In order to investigate the versatility of the catalyst, we carried out the oxidation using a range of alcohols in the absence of amines under atmospheric air. *para*- substituted benzyl alcohols reacted efficiently to furnish the corresponding aldehydes in excellent isolated yields (Table 3, entries 1 and 3). On the other hand, *meta*- and *ortho*- substituted alcohols afforded corresponding imines in good to moderate yields (Table 3, entries 4 - 7). The formation of aldehyde clearly indicates that imination proceeds via an initial oxidation step.

Table 3. Aerobic oxidation of Alcohols to Aldehydes[a]

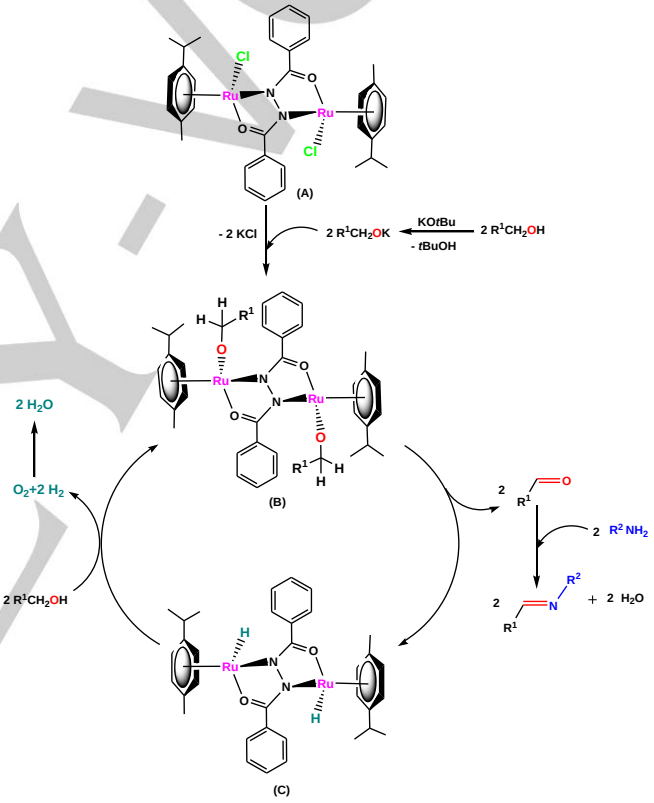


1 4

Entry	1	4	Yield %[b]
1		 :(4a)	98
2		 :(4b)	96
3		 :(4c)	89
4		 :(4d)	78
5		 :(4e)	73
6		 :(4f)	66
7		 :(4g)	71

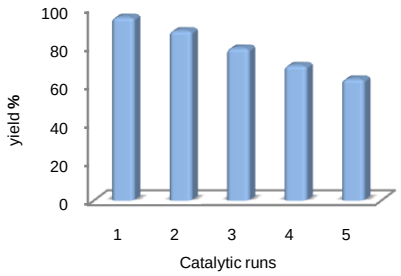
[a] [a] Reaction conditions: 1 (1 mmol), catalyst **4** (1 mol %), t-BuOK (10 mol %), 4 Å molecular seives and THF (5 mL) stirred at r.t. for 24 h in open air. [b] Isolated yields.

The excellent selectivity of the diruthenium arene catalyst in the aerobic imine synthesis encouraged us to propose a plausible mechanism. As shown in scheme 3, the imination process is believed to be initiated by the formation of ruthenium−alkoxide species (B) from the diruthenium arene complex (A). Further, β-hydride abstraction by complex (B) produces ruthenium−hydride complex (C) by releasing the aldehyde intermediate (Table 3) which further reacts with amines to produce imines with the elimination of water. Complex (C) enters into the next catalytic cycle by forming (B) with the release of water.



Scheme 3. Plausible Mechanism for Imination

The life span and level of reusability of a catalytic system are crucial factors in homogeneous catalysis.[13] Although recovery of homogeneous catalyst from the reaction mixture has some drawbacks, we made an effort to recover and reuse the present catalytic system in further cycles. *N*-(4-methoxybenzylidene)-4-methoxybenzenamine obtained by the coupling of 4-methoxy benzyl alcohol and *p*-anisidine was extracted after the completion of the reaction. The catalyst was recovered from the reaction mixture and reused for the next cycle. Thus, we found that the catalyst remains active up to five consecutive runs with gradual decrease in the activity from 95 to 63%.



Conclusions

In conclusion, we have synthesized and characterized a new air stable arene diruthenium(II) complexes. Further, the complexes were developed as catalysts for the selective aerobic synthesis of imines from various alcohols and amines producing water as the only byproduct. The oxidative imination preceded efficiently using the catalyst **4** with 1 mol% catalyst loading at room temperature under aerobic conditions. The current system tolerates a wide range of substrates and afforded imines in good to excellent yields. In addition, selective aerobic oxidation of alcohols to aldehydes was also arrived in order investigate the underlying mechanism and to test the versatility of the catalytic system. Hence, the scientific value of this methodology is proved by the development of non-pincer type diruthenium(II) catalysts for the direct synthesis of imines and detailed mechanistic studies are underway.

Experimental Section

General method for the synthesis of the arene diruthenium(II) complexes (4-6): $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (1 equiv.) and N-Benzoylbenzohydrazide **1** (1 equiv.), or N-Benzoyl-4-chlorobenzohydrazide **2** (1 equiv.), or N-Benzoyl-4-methoxybenzohydrazide **3** (1 equiv.) were dissolved in 25 mL of toluene and refluxed for 2h. The solution was concentrated to 2 mL under reduced pressure, and addition of petroleum ether (60−80 °C) in excess gave a clear orange solid. The product was collected by filtration, washed with petroleum ether, and dried in vaccuo.

Synthesis of dinuclear $[(\eta^6\text{-}p\text{-Cymene})_2Ru_2Cl_2(\mu\text{-L1})]$ (4): Orange Solid. Yield: 93% ; Found: C, 52.22; H, 4.89; N, 3.58%. Calc. for $C_{34}H_{38}Cl_2N_2O_2Ru_2$: (779.72 g mol^{-1}): C, 52.37; H, 4.91; N, 3.59%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm), 7.97 (m, 4 H, ArH), 7.45 (m, 6 H, ArH), 5.12 (d, $^3J_{H-H}$ = 6 Hz, 2H, CH *p*-cym), 5.00 (d, $^3J_{H-H}$ = 6 Hz, 2H, CH *p*-cym), 4.52 (d, $^3J_{H-H}$ = 5.6 Hz, 2H, CH *p*-cym), 3.72 (d, $^3J_{H-H}$ = 5.6 Hz, 2H, CH *p*-cym), 2.61 (sept, 2H, CH(CH3)2), 2.13 (s, 6H, CH_3), 1.11 (t, $^3J_{H-H}$ = 6.4 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm), 172.7, 136.58, 129.80, 129.43, 127.84, 99.96, 99.87, 83.38, 81.50, 79.96, 79.91, 30.40, 22.43, 22.36, 18.74. FT-IR (cm^{-1}). 1540, 1485, 1393, 1036. UV-vis (CH_2Cl_2, λ_{max} nm; ε dm^3 mol^{-1} cm^{-1}): 456 (670), 328 (3,700), 230 (11,000). HR-ESI-MS m/z [Found (Calcd)]: 739.1068 (739.1047) {[M – Cl – HCl]$^+$ ≡ [$C_{34}H_{38}ClN_2O_2Ru_2$]$^+$}

Synthesis of dinuclear $[(\eta^6\text{-}p\text{-Cymene})_2Ru_2Cl_2(\mu\text{-L2})]$ (5): Orange Solid. Yield: 85%; Found: C, 50.12; H, 4.63; N, 3.40%. Calc. for $C_{34}H_{37}Cl_3N_2O_2Ru_2$: (814.17 g mol^{-1}): C, 50.16; H, 4.58; N, 3.44%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm), 7.90 (m, 4 H, ArH), 7.40 (m, 5 H, ArH), 5.05 (d, 2H, $^3J_{H-H}$ = 6.4 Hz, CH *p*-cym), 4.96 (d, $^3J_{H-H}$ = 6.4 Hz, 2H, CH *p*-cym), 4.48 (d, $^3J_{H-H}$ = 6 Hz, 2H, CH *p*-cym), 3.80 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH *p*-cym), 3.63 (d, $^3J_{H-H}$ = 6 Hz, 1H, CH *p*-cym), 2.52 (sept, 2H, CH(CH3)2), 2.09 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.05 (m, $^3J_{H-H}$ = 7.6 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm),172.96, 171.77, 136.48, 135.61, 134.92, 131.44, 129.76, 129.50, 128.01, 127.86, 100.22, 100.17, 100.09, 99.88, 83.40, 81.57, 79.96, 79.92, 79.82, 30.46, 30.41, 22.58, 22.38, 22.35, 22.26, 18.80 18.75. FT-IR (cm^{-1}). 1534, 1483, 1386, 1034. UV-vis (CH_2Cl_2, λ_{max} nm; ε dm^3 mol^{-1} cm^{-1}): 460 (630), 325 (4,300), 229 (10,700). HR-ESI-MS m/z [Found (Calcd)]: 745.0551 (745.0708) {[M–Cl – HCl]$^+$ ≡ [$C_{34}H_{36}N_2O_2ClRu_2$]$^+$}

Synthesis of dinuclear $[(\eta^6\text{-}p\text{-Cymene})_2Ru_2Cl_2(\mu\text{-L3})]$ (6): Orange Solid. Yield: 89%; Found: C, 51.84; H, 5.01; N, 3.47%. Calc. for $C_{35}H_{40}Cl_2N_2O_3Ru_2$: (809.75 g mol^{-1}): C, 51.91; H, 4.98; N, 3.46%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm), 7.96 (m, 4 H, ArH), 7.45 (m, 3 H, ArH), 6.96 (d, $^3J_{H-H}$ = 8 Hz, 2H, ArH), 5.11 (m 2H, CH *p*-cym), 5.00 (m 2H, CH *p*-cym), 4.55 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH *p*-cym), 4.50 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH *p*-cym), 3.93(d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH *p*-cym), 3.87(s, 3H, O-CH_3), 3.70 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH *p*-cym), 2.61 (sept, 2H, $CH(CH_3)_2$), 2.17 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.11 (m, $^3J_{H-H}$ = 6 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm),172.73, 172.48, 160.44, 136.56, 129.32, 128.96, 128.27, 127.73, 113.01, 99.95, 99.86, 99.58, 83.47, 83.04, 81.73, 81.49, 79.93, 79.86, 79.82, 55.41, 45.9, 30.33, 30.31, 22.55, 22.32, 22.19, 18.71, 18.68. FT-IR (cm^{-1}). 1537, 1487, 1386, 1032. UV-vis (CH_2Cl_2, λ_{max} nm; ε dm^3 mol^{-1} cm^{-1}): 458 (600), 329 (4,500), 228 (10,900). HR-ESI-MS m/z [Found (Calcd)]: 709.0955 (709.0941) {[M – Cl – HCl]$^+$ ≡ [$C_{35}H_{39}N_2O_3Ru_2$]$^+$}

Typical procedure for diruthenium-catalyzed aerobic synthesis of imines from alcohols and amines: The mixture of alcohol (1 mmol), an amine (1 mmol), *t*-BuOK (10 mol%), catalyst (1 mol%), 4 Å molecular sieves was stirred in the open air at room temperature (ca. 25–30 ^{0}C) and monitored by TLC/ GC-MS until completion. After completion of the reaction, the reaction mixture was filtered and the solvent was evaporated under reduced pressure. Then the resulting residue was purified by silica gel column chromatography using EtOAc:hexane to afford imine products.

Typical procedure for diruthenium-catalyzed selective oxidation alcohols to aldehydes: The mixture of alcohol (1 mmol), *t*-BuOK (10 mol%), catalyst (1 mol%), 4 Å molecular sieves was stirred for 24 h in the open air at r.t. in 5 mL THF and monitored by TLC. The reaction mixture was filtered and the solution was evaporated under reduced pressure and then subjected to silica gel column chromatography using EtOAc:hexane to afford aldehyde products.

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Keywords: Diruthenium • Aerobic • Imines • Aldehydes • Green synthesis

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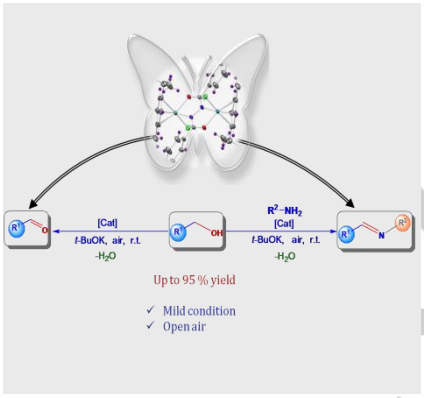
Entry for the Table of Contents

Organoruthenium mediated synthesis

FULL PAPER

Newly synthesized arene diruthenium(II) complexes were used as efficient catalysts for the selective synthesis of imines under mild conditions. The reaction operates in the presence of green and economic air as oxidant with the release of water as the only by-product.



Sundar Saranya, Rengan Ramesh and Jan Grzegorz Małecki*

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One-pot Catalytic Approach for the Selective Aerobic Synthesis of Imines from Alcohols and Amines using Efficient Arene Diruthenium(II) Catalysts under Mild Condition