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Ligand controlled switchable selectivity in ruthenium catalyzed aerobic oxidation of primary amines

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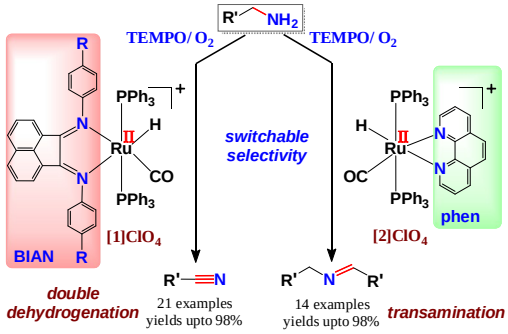
A ligand controlled catalytic system for the aerobic oxidation of 1° amines to nitriles and imines has been developed where the varying π-acidic feature of BIAN versus phen in the frameworks of the ruthenium catalysts attribute to the switchable selectivity.

Development of novel strategies for amine oxidation to nitriles or imines is important largely due to their pervasiveness as intermediates in accessing other functionalities and their wide applicability as synthons in industry.[1] In general, primary amine oxidation involves two competing, dehydrogenation and transamination pathways. The amine substrate can either undergo double dehydrogenation to a nitrile or single dehydrogenation to an aldimine intermediate followed by the nucleophilic attack of a second amine molecule affording a bimolecular imine as the product. Recent findings have unveiled that it is indeed the nature of the catalytic system that plays a prominent role in altering the predicted selectivity.[2,3] For example, recently Stahl reported selective formation of nitriles in presence of a Cu^{I}/TEMPO catalytic system[2a] in contrast to earlier reported Cu/nitroxyl systems which were found to be effective towards the formation of bimolecular imines.[3c-e] Alternatively, aerobic oxidation of amines was demonstrated by Bäckvall involving a ruthenium transfer hydrogenation catalyst (the Shvo's catalyst) in combination with an electron-rich quninone (2,6-dimethoxy-1,4-benzoquinone) and a Co(salen) cocatalyst, where the system was selective only towards the oxidation of 2° amines to imines.[3k] However, selective generation of nitriles or imines from identical substrates (1° amines) by utilizing catalyst rather than substrate control has remained unexplored so far.[4] Herein we report a series of newly synthesized ruthenium hydrido complexes $[Ru^{II}(R\text{-}BIAN)(PPh_3)_2(CO)(H)]ClO_4$[5] incorporating BIAN (R= OMe (**1a**$^+$), Me (**1b**$^+$), H (**1c**$^+$), Cl (**1d**$^+$), NO_2 (**1e**$^+$)) as efficient catalysts towards selective oxidation of primary amines to nitriles in presence of a catalytic amount of TEMPO (2,2′,6,6′-tetramethylpiperidine *N*-oxyl) under aerobic conditions (Scheme 1). Interestingly, a complete reversal in selectivity is achieved with moderately π-acidic 1,10-phenanthroline (phen) coordinated analogous ruthenium-hydrido complex, (Scheme 1).



Scheme 1. An outline of the present work.

Such a ligand controlled selectivity can be attributed to the varying redox feature of BIAN[6] versus phen.[7] To our knowledge, the present work represents the first example of a ligand controlled selective dehydrogenation of primary amines to nitriles and homocoupled imines with two analogous BIAN and phen ligated ruthenium-hydrido complexes as catalysts, respectively. The novelty of the present work is further highlighted through successful tolerance of a wide variety of benzylic and aliphatic amines under *aerobic conditions* affording nitriles or imines in good yields with special reference to the earlier reports on ruthenium catalyzed amine oxidation which in most cases required inert atmosphere and harsh reaction conditions[8] or efficacy of the systems is constrained by very limited substrates scope.[2e-j]

For optimization of the critical reaction parameters, benzylamine (**3a**) was chosen as the model substrate and toluene as the solvent. Initial reaction with [**1a**]ClO_4 as the catalyst resulted in nitrile (**4a**) and homocoupled imine (**5a**) in comparable yields (entry 1, Table 1) with slight amount of unreacted amine. Interestingly, addition of a catalytic amount of TEMPO (10 mol%) resulted in a selective increase in the yield of nitrile (entry 2, Table 1). An efficient oxidation protocol in favor of the double dehydrogenation of amine to nitrile was realized in presence of 2 mol% [**1a**]ClO_4 as the catalyst in combination with 20 mol% TEMPO under O_2 balloon pressure, affording benzonitrile in 76% yield (entry 3, Table 1). However, an increase in the amount of TEMPO upto 30 mol% did not alter the yield to an appreciable extent (entry 4, Table 1). A systematic screening of solvents revealed toluene to be ideal for the selective formation of nitriles (entries 5-8, Table 1).

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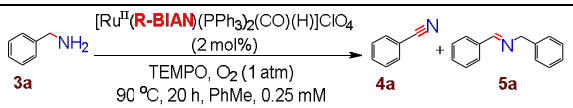
Table 1 Optimization of the reaction parameters for nitrile formation[a]



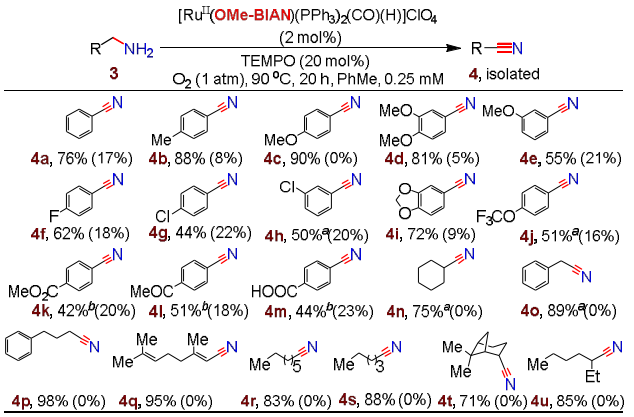
entry	catalyst	solvent	yield (%)	
			4a	**5a**
1	[**1a**]ClO$_4$	PhMe	47	45
2[b]	[**1a**]ClO$_4$/TEMPO	PhMe	70	24
3	**[1a]ClO$_4$/TEMPO**	**PhMe**	**76**	**17**
4[c]	[**1a**]ClO$_4$/TEMPO	PhMe	78	21
5	[**1a**]ClO$_4$/TEMPO	PhCF$_3$	3	8
6	[**1a**]ClO$_4$/TEMPO	THF	3	10
7	[**1a**]ClO$_4$/TEMPO	ACN	2	10
8	[**1a**]ClO$_4$/TEMPO	dioxane	10	5
9	[**1b**]ClO$_4$/TEMPO	PhMe	65	21
10	[**1c**]ClO$_4$/TEMPO	PhMe	64	21
11	[**1d**]ClO$_4$/TEMPO	PhMe	71	20
12	[**1e**]ClO$_4$/TEMPO	PhMe	73	18
13[d]	[**1a**]ClO$_4$	PhMe	16	36
14[d]	[**1a**]ClO$_4$/TEMPO	PhMe	23	32
15	TEMPO	PhMe	-	-

[a]Reaction conditions: catalyst (2 mol%), benzylamine (0.75 mmol), TEMPO = 20 mol% in toluene (3 mL) at 90 °C under O$_2$ (1 atm, balloon). [b] TEMPO = 10 mol%. [c]TEMPO = 30 mol%. [d]Reaction was performed under N$_2$ atmosphere. GC yields were calculated using 1,3,5-Trimethoxybenzene as an internal standard.

Additionally, screening with differently substituted BIAN coordinated ruthenium-hydrido complexes as catalysts ([**1b-1e**]ClO$_4$) afforded nitrile in comparable yields which essentially nullifies the impact of the electron donating or withdrawing substituents in the BIAN moiety in modifying the catalytic activity of the complex (entries 9-12, Table 1).[9] As expected, a control experiment in absence of the metal catalyst resulted in zero conversion of the amine substrate (entry 15, Table 1).

Subsequently, the optimized reaction conditions were applied to a wide variety of primary amines to assess the scope and limitations of the present protocol (Table 2). Most notable feature was the excellent conversion of the long chain aliphatic amines selectively to their respective nitriles (**4n-u**) without the formation of any imine byproducts. This implies that the alkyl groups of nonfunctionalized aliphatic substrates reinforced high degree of nucleophilicity on the nitrogen center and thereby facilitated its coordination to the electrophilic metal center. Similar was the observation for aryl rings substituted with strongly electron donating groups at the *para* position (**4b-d**).[3k,10] On the contrary, a decrease in yield of the desired nitrile was evident in electrically neutral or even an alkoxy substituted benzyl amine at the *meta* position (**4a**, **4e**). As expected, benzylamine substituted with –OCF$_3$, -CO$_2$Me, -COMe or -COOH group at the *para* position resulted in nitrile albeit in low yield (**4j-m**). The relatively low yields of the products in such cases can be attributed to the less nucleophilic reactive nitrogen centers which hindered the coordination of the amine substrates to the electrophilic metal center and thereby leading to unreacted starting amines and bimolecular imine byproducts in ~1:1 ratio at the end of the reaction. Aryl halides were found to be compatible without any dehalogenation process (**4f-h**). The versatility of the protocol was further extended through the selective oxidation of piperonylamine to its corresponding nitrile in moderately good yield (**4i**). Heterocyclic substrates were found to be inactive with this protocol (not shown) which might be due to coordination of the heteroatoms to the metal center

Table 2 Substrates scope for [**1a**]ClO$_4$ catalyzed oxidation of primary amines to nitriles



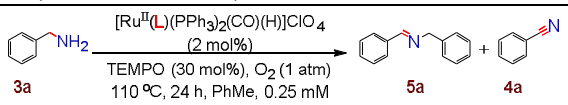
Unless otherwise stated, yields refer to isolated products. Yields of the respective imines are given in parentheses. [a]GC yields were calculated using 1,3,5-Trimethoxybenzene as an internal standard. [b]Reaction was carried out at 120 °C and with 30 mol% TEMPO.

leading to deactivation of the catalyst.[11]

Unlike [**1a**]ClO$_4$ catalyzed nitrile formation, [**2**]ClO$_4$ catalyzed bimolecular imine formation from primary amines was achieved with ~100% selectivity (entry 5, Table 3). This underscores the highly selective nature of the active catalytic species [**2**]ClO$_4$ in favor of transamination instead of any double dehydrogenation to yield nitriles. Screening with [**1a**]ClO$_4$ and other analogous ruthenium-hydrido complexes coordinated to 2,2′-bipyridine (bpy) and isoquinoline (isoQ) having comparable π-acidity to phen, established the superiority of the latter (entries 1-3, Table 3). Besides, no reaction took place either in the absence of TEMPO (entry 6, Table 3) or the metal catalyst (entry 8, Table 3) which essentially indicates the presence of both the components being crucial for bimolecular imine formation.

The substrates scope was evaluated for [**2**]ClO$_4$ catalyzed transamination reaction (Table 4). Unsubstituted, halogenated as well as alkyl or alkoxy substituted benzyl amines underwent clean conversion in good to excellent yields (**5a-g, 5m**). The intriguing feature was the effective oxidation of benzylic amines substituted with electron withdrawing, -CF$_3$, -OCF$_3$, -CO$_2$H, -CO$_2$Me and -COMe groups to their respective imines (**5h-l**) which otherwise gave poor

Table 3 Optimization of the reaction parameters for imine formation[a]



entry	catalyst	yield (%)	
		5a	**4a**
1[c]	[**1a**]ClO$_4$	33	68
2[b]	[Ru(bpy)(PPh$_3$)$_2$(CO)(H)]ClO$_4$	45	15
3[b]	[Ru(isoQ)(PPh$_3$)$_2$(CO)(H)]ClO$_4$	44	54
4[b]	[Ru(phen)(PPh$_3$)$_2$(CO)(H)]ClO$_4$	58	3
5[c]	**[Ru(phen)(PPh$_3$)$_2$(CO)(H)]**ClO$_4$	**98**	**-**
6[d]	[Ru(phen)(PPh$_3$)$_2$(CO)(H)]ClO$_4$	-	-
7[e]	[Ru(phen)(PPh$_3$)$_2$(CO)(H)]ClO$_4$	20	-
8[c]	no catalyst	-	-

[a]Reaction conditions: catalyst (2 mol%), benzylamine (0.75 mmol) in toluene (3 mL) at 110 °C under O$_2$ (1 atm, balloon). [b]TEMPO = 20 mol%. [c]TEMPO = 30 mol%. [d]Reaction in absence of TEMPO. [e]Reaction was performed under N$_2$ atmosphere. GC yields were calculated using 1,3,5-Trimethoxybenzene as an internal standard.

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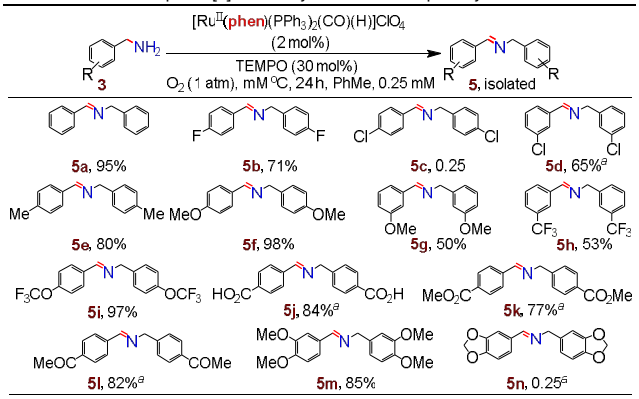
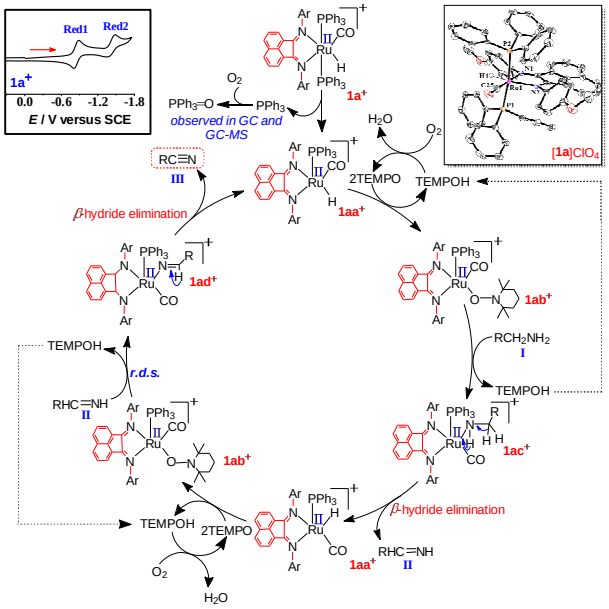
Table 4 Substrates scope for [**2**]ClO_4 catalyzed oxidation of primary amines to imines.



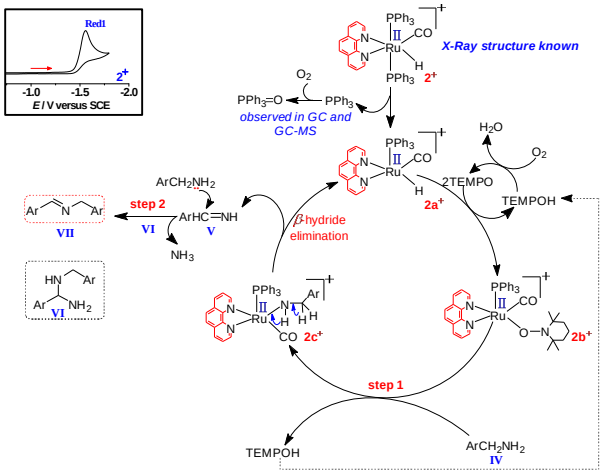
Unless otherwise stated, yields refer to isolated products. [a]GC yields were calculated using 1,3,5-Trimethoxybenzene as an internal standard.

(**4j-m**) or no conversion to nitriles (not shown) with [**1a**]ClO_4 as the catalyst. Piperonylamine gave moderate yield of the respective imine under the present reaction conditions (**5n**). Unfortunately, aliphatic primary amine substrates were left completely unreacted under this reaction conditions (not shown).

Based on experimental observations and kinetic studies, two plausible mechanistic pathways for the oxidation of primary amines to nitriles and imines are depicted in Schemes 2 and 3, respectively. A set of control experiments (entries 1-4, Table 1 and entries 4-6, Table 3) revealed that TEMPO had a major role to play in each case, although it alone failed to afford any product in the absence of ruthenium catalysts (entry 15, Table 1 and entry 8, Table 3). In either case, TEMPO behaves as an electron transfer mediator which facilitates a low-energy electron transfer from the amine to molecular oxygen. Similar mechanisms for aerobic oxidation of alcohol and amines were earlier reported by Sheldon and Bäckvall involving ruthenium centered dehydrogenation in the presence of hydrogen- and electron-transfer agents, such as TEMPO[11] and benzoquinone,[3k-m] respectively. [**1a**]ClO_4 was unambiguously characterized by X-ray crystallography, UV-vis, CV, ESI-MS and NMR analysis (see ESI for details). Detailed analysis of [**2**]ClO_4 is previously reported in literature.[12] Both pathways involve the initial dissociation of one PPh_3 ligand, analogous to earlier reported alcohol oxidation processes,[13] to form coordinatively unsaturated complex, **1aa**$^+$ or **2a**$^+$. This was substantiated through detection of free PPh_3 or PPh_3=O by GC-MS within 5 mins of the reaction before any significant production of nitrile or imine. An alternate possibility of an ruthenium-oxo intermediate formation is less likely in the present case[13] since both the reactions were operational under N_2 atmosphere (entry 14, Table 1 and entry 7, Table 3). In either case, there is an initial formation of a ruthenium-amido intermediate, (**1ac**$^+$ or **2c**$^+$) which undergoes β-hydride elimination in the subsequent step to generate an aldimine intermediate (**II** or **V**). It is ratioanlized that in the presence of strongly π-accepting BIAN, as was also evident from the relatively low first reduction potential of the BIAN in **1a**$^+$ (E^0_{pc} = –0.85 V for **1a**$^+$, Scheme 2 and Table S6, ESI), the Lewis acidity of the metal center is enhanced. This eventually facilitates a faster formation of the ruthenium-imido intermediate (**1ad**$^+$) and a concomitant β-hydride elimination to form the desired nitrile (**III**), selectively.[3k] On the contrary, the complete reversal in center in presence of a moderately π-acidic phen (first reduction selectivity with [**2**]ClO_4 as the catalyst resulting in bimolecular imine formation (**V**), might be due to the relatively less electrophilic metal potential of phen in **2**$^+$ was found to be E^0_{pc} = –1.5 V, Scheme 3).



Scheme 2. Plausible mechanism for [**1a**]ClO_4 catalyzed nitrile formation.



Scheme 3. Plausible mechanism for [**2**]ClO_4 catalyzed imine formation.

There is an initial dehydrogenation from **IV** to **V**, however **V** being relatively less nucleophilic is attacked by a second amine molecule to afford an aminal intermediate (**VI**) which subsequently undergoes NH_3-removal to yield homocoupled imine (**VII**) as the final product.[3k]

A product formation plot of the yield of nitrile and imine versus time with [**1a**]ClO_4 as the catalyst, exhibits the faster rate of nitrile formation in comparison to imine which is usually observed as a byproduct under the standard reaction conditions for nitrile formation (Figure S15, ESI). The reaction follows a first order rate kinetics with respect to the amine substrate both for nitrile and imine formation (see ESI for details). In addition, a primary kinetic isotope effect (KIE), k_H/k_D = 1.7 is observed in [**1a**]ClO_4 catalyzed nitrile formation (Figure 1a) in contrast to a secondary KIE, k_H/k_D = 0.24 in [**2**]ClO_4 catalyzed transamination reaction (Figure 1b), which collectively implies that benzylic C–H bond cleavage of the amine is probably turnover limiting in the former in comparison to the latter one. The inverse KIE can be ascribed to a change in hybridization of

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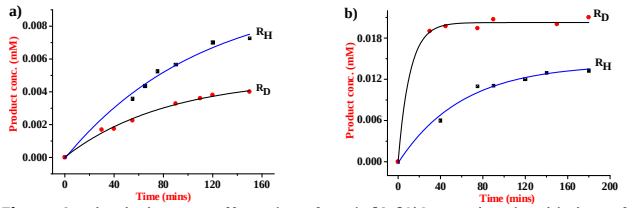

Figure 1. Kinetic isotope effect data for a) [**1a**]ClO_4 catalyzed oxidation of $PhCH_2NH_2$ and isotopically labeled $PhCD_2NH_2$ to nitrile, b) [**2**]ClO_4 catalyzed oxidation of $PhCH_2NH_2$ and isotopically labeled $PhCD_2NH_2$ to imine.

the same C–H bond from sp^2 to sp^3 on attack of the second amine molecule resulting in an aminal intermediate **VI**.[14] Hammett studies further predict a positively charged transition state in [**1a**]ClO_4 catalyzed nitrile formation (ρ = –3.3, Figure 2a) while a change in rate determining step as a function of various substituents is operational in [**2**]ClO_4 catalyzed imine formation (Figure 2b).[15] The abrupt change in the slope of the plot with two intersecting lines for [**2**]ClO_4 catalyzed imine formation indicates that electron-withdrawing groups are assisting step 1, making step 2 rate-limiting and alternatively, electron-donating groups increase the rate of step 2, making step 1 rate-determining (*cf.* Scheme 3).

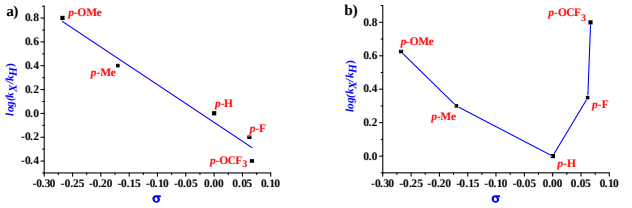

Figure 2. Hammett plot: [$log(k_X/k_H)$] versus σ for competitive oxidation of benzyl amine and *p*-substituted benzyl amines for a) [**1a**]ClO_4 catalyzed oxidation to nitrile, b) [**2**]ClO_4 catalyzed oxidation to imine.

In conclusion, the present communication demonstrates for the first time a ligand controlled catalytic system for the simultaneous formation of nitriles and imines from primary amines as substrates. Interestingly, such switchable selectivity can be attributed to the varying π-acidic feature of BIAN versus phen in the frameworks of the catalysts. Overall, both the catalysts exhibit excellent functional group compatibility; a wide variety of benzylic and aliphatic primary amines were well-tolerated under the present reaction conditions. Reports on ruthenium catalyzed aerobic oxidation of amines are scarce and therefore, the present protocols provide excellent alternatives to the traditional procedures.

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