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Extending the Chemistry of Hexamethylenetetramine in Ruthenium-Catalyzed Amine Oxidation

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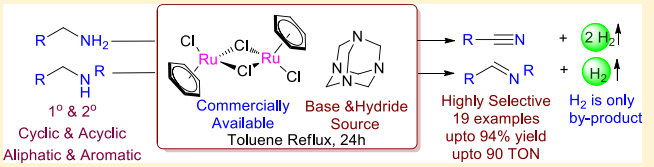
Supporting Information

ABSTRACT: A very efficient, highly atom economical, and environmentally benign oxidation of primary and secondary amines using an in situ catalyst system generated from commercially available ruthenium(II) benzene dichloride dimer and hexamethylenetetramine has been demonstrated. Mechanistic studies revealed that hexamethylenetetramine acted as a source of hydride to generate the active ruthenium hydride catalyst and amine oxidation involves a dehydrogenative pathway. In comparison to reported catalyst systems for the dehydrogenative oxidation of amines, this synthetic protocol makes use of a simple ruthenium precursor and a cheaper additive; it is very selective, leading to the exclusive formation of nitrile/imine compounds. Further, it releases hydrogen as the only side product, suggesting the potential application of the developed catalyst system in hydrogen storage.



INTRODUCTION

Nitrile and imine groups are considered as very important functional groups because they act as key building blocks for the synthesis of several organic compounds such as carboxylic acids, amines, amides, and heterocyclic compounds and several industrially important products such as pharmaceuticals, dyes, pesticides, polymers, etc.[1,2] The development of efficient, selective, cost-effective, and environmentally friendly catalyst systems for the synthesis of nitrile and imine compounds has always been one of the biggest pursuits of the scientific community.[3,4] Conventional methods available for synthesizing nitrile compounds include the ammoxidation method,[5a] the Sandmeyer type reaction,[5b,c] the Rosenmund−von Braun reaction,[5d] dehydration of aldoximes and amides,[6] and metal-catalyzed cyanation.[7] Nitriles are also being synthesized from alcohols, aldehydes, and azides.[8] On the other hand, the traditional synthesis of imines involves the oxidation of secondary amines using sacrificial amounts of oxidizing agents such as IBX, DDQ, MnO_2, sulfur, HgO-I_2, and many others.[9] Many metal-based heterogeneous and homogeneous catalyst systems are also known to catalyze the oxidation of secondary amines.[10] Though a plethora of methods are available for the syntheses of both imine and nitrile compounds from a variety of starting materials, most of the methods suffer from at least one of the following drawbacks: (a) use of toxic reagents, (b) poor atom economy, (c) harsh reaction conditions, and (d) poor selectivity.[3−10]

Transition-metal-catalyzed oxidation of amines to form nitriles and imines has been considered as one of the most suitable synthetic methods and is known to follow two different pathways. The synthetic methodology which involves aerobic oxidation of amines works in the presence of a transition metal in tandem with an oxygen molecule or some other oxygen source and produces water as the side product.[11] Though this method produces nitriles and imines in excellent yields, sometimes it suffers with selectivity issues and is known to produce an amide as the side product.[11a]

An alternative approach that employs transition-metal complexes for the dehydrogenative oxidation of amines with the evolution of hydrogen as the sole byproduct has been found to be an effective methodology. Observing the dehydrogenative oxidation of amines in the absence of a hydrogen acceptor is considered to be superior in comparison to aerobic oxidation and other traditional methods due to high atom economy and greener nature. Notable examples of ruthenium complexes that are known to catalyze acceptorless dehydrogenative oxidation of secondary amines to imines are $RuH_2(CO)(PPh_3)_3$ and Shvo's catalyst systems reported by Hong and co-workers and a Ru(II)-NNC pincer complex used by Wang et al.[12] In comparison to the dehydrogenation of secondary amines, reports on the double dehydrogenation of primary amines to produce nitriles are very scarce. To the best of our knowledge, there is only one report available on ruthenium-catalyzed base-free, acceptorless double dehydrogenation of primary amines to afford nitriles using an NNN-Ru(II) hydride system reported by Szymczak and co-workers (Figure 1).[13a,b] Recently, Bera and co-workers reported an efficient ruthenium pyrazole/$KOBu^t$ system for the acceptorless dehydrogenation of primary amines into nitriles (Figure 1).[13c]

The role of additives in transition-metal-catalyzed organic transformations is very crucial in deciding the overall catalytic activity and selectivity of the catalyst. It is recognized that additives in catalysis often play vital roles in activating the substrate and/or in generating/regenerating the active catalyst.

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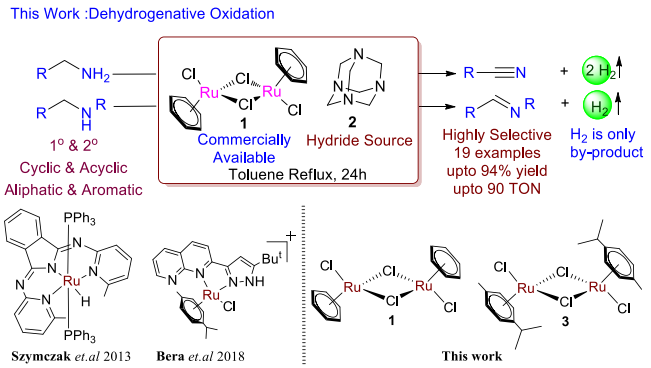


Figure 1. Ruthenium-catalyzed amine dehydrogenation and examples of ruthenium complexes used for double-dehydrogenative oxidation of primary amines.

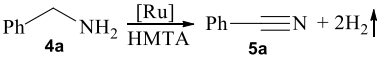
The nature of the additives used in the literature varies from inorganic acids and bases to metal salts, and their amount ranges from catalytic to stoichiometric quantities.[14] Apart from the above examples, several nitrogen-based compounds, including hexamethylenetetramine (HMTA), have also been used as additives in the literature.[14d] HMTA and its derivatives are being used in chemical synthesis not only because of their solubility in water and in a variety of organic polar solvents but also for their simple operation, mild conditions, and environmental friendliness.[15] HMTA is a well-known methylating agent and is used in the synthesis of several industrially important products, including Bakelite.[15,16] In a seminal report Fu and his co-workers have reported the use of HMTA as both a ligand and a reducing agent in copper-catalyzed AGET-ATR batch emulsion polymerization.[16c] Recently, Qiang and co-workers have utilized HMTA as a single source of carbon and nitrogen for the synthesis of N-doped graphenes.[17] Notwithstanding its potential application as a reducing and methylating agent, HMTA has rarely been used in catalysis[15e,16,17] and to the best of our knowledge HMTA and its derivatives have not been used as the source of a hydride group.

Herein, we report a very efficient and greener process for the synthesis of nitriles and imines using an in situ catalyst system developed from commercially available ruthenium(II) benzene dichloride dimer (**1**) and hexamethylenetetramine (**2**) (Figure 1). We also gathered several pieces of experimental evidence to strongly indicate that this work represents the first example of the use of HMTA in catalysis as an additive and hydride donor.

RESULTS AND DISCUSSION

Currently, our group is involved in developing water-soluble ruthenium catalysts using the 1,3,5-phosphaadamantane (PTA) ligand.[18] We have observed that the inadvertent presence of HMTA (**2**) as an impurity in PTA played a role in ruthenium-catalyzed oxidation reactions, which prompted us to employ HMTA (**2**) in the field of catalysis. We have chosen ruthenium-catalyzed conversion of benzylamine (**4a**) to benzonitrile (**5a**) as a model reaction, and several reactions were tried to optimize the reaction conditions, as summarized in Table 1. Primarily, 5 mol % of ruthenium(II) benzene dichloride dimer (**1**) and ruthenium(II) *p*-cymene dichloride dimer (**3**) were tested in the absence of any additive under open conditions to nitrogen, using toluene as the solvent at 110 °C for 24 h, which afforded **5a** in poor yields (Table 1, entries 1 and 2). When compounds **1**, **3**, and $RuCl_3 \cdot nH_2O$ (**4**) were tested in the presence of HMTA (**2**), benzonitrile (**5a**)

Table 1. Optimization of Reaction Conditions



entry	[Ru]	[Ru] (mol %)	HMTA (mol %)	solvent	temp (°C)	time (h)	yield (%) (TON)[a]
1	**1**	5		toluene	110	24	19
2	**3**	5		toluene	110	24	22
3	**1**	5	5	toluene	110	24	96 (19)
4	**3**	5	5	toluene	110	24	70
5	**4**	5	5	toluene	110	24	43
6			5	toluene	110	24	
7	**1**	5	2.5	toluene	110	24	46
8	**1**	4	4	toluene	110	24	94(24)
9	**1**	3	3	toluene	110	24	90(30)
10	**1**	2	2	toluene	110	24	96(48)
11	**1**	1	1	toluene	110	24	74(74)
12	**1**	0.5	0.5	toluene	110	24	45(90)
13	**1**	2	2	THF	64	24	9
14	**1**	2	2	DCM	40	24	1
15	**1**	2	2	toluene	80	24	40
16	**1**	2	2	toluene	110	6	29
17	**1**	2	2	toluene	110	12	57

[a]GC yield using dodecane as internal standard and average of at least two runs.

was obtained as the product in excellent and moderate yields, respectively (entries 3−5). In order to test the role of ruthenium in the formation of **5a**, we performed the reaction under identical conditions: however, the reaction was carried out in the absence of any ruthenium compound, which did not yield the product **5a** (entry 6). After identifying compound **1** as the suitable precatalyst, we optimized the ratio between **1** and **2** and found that a 1:1 equiv ratio was ideal for dehydrogenation of **4a**, as a further change in ratio resulted in a diminished yield of **5a** (entry 7). In view of decreasing the catalyst loading, several reactions were tried with 4, 3, 2, 1, and 0.5 mol % of **1** and **2**, and 2 mol % was found to be suitable for obtaining **5a** in excellent yield (entries 8−12); however, the highest turnover number of 90 was obtained when 0.5 mol % of **1** and **2** was used (entry 12). The reaction solvent, temperature, and time were also optimized, and it was found that toluene reflux conditions for 24 h were ideal for double dehydrogenation of **4a** to form the product **5a** in excellent yield (entries 13−17).

Having the optimized reaction conditions in hand, we expanded the substrate scope of our catalyst system for the double-dehydrogenative oxidation of several primary amines into nitriles, as summarized in Table 2. As a beginning, the electronic and steric effects of various substituents on benzylamine were explored. The presence of electron-donating groups such as methyl (**4b**) and methoxy (**4c**) groups on the para position of benzylamine afforded the nitrile products **5b**,**c**, respectively, in excellent yields (entries 2 and 3). On substitution of the para position with electron-withdrawing groups such as chloro (**4d**), fluoro (**4e**), and nitro (**4f**) groups, the product yields decreased slightly (entries 4−6). To check the chemoselective nature of our catalyst system, double dehydrogenation of 4-aminobenzylamine (**4g**) having both H_2N-CR_2 and H_2N-CH_2- groups (entry 7) was conducted. It was found that under the given experimental conditions our catalyst system yielded 4-aminobenzonitrile (**5g**) as the only

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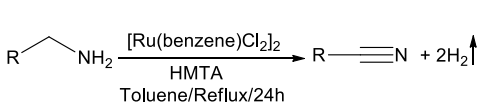
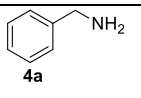
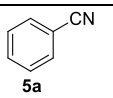
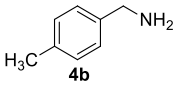
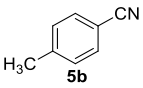
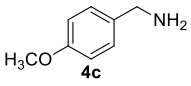
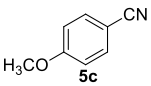
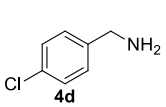
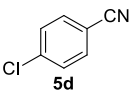
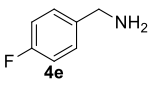
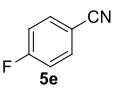
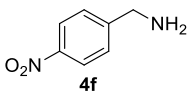
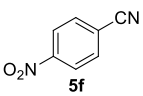
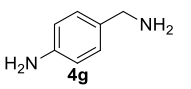
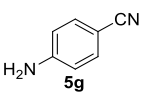
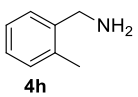
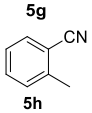
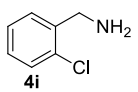
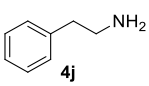
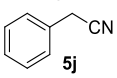
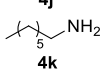
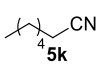
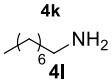
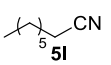
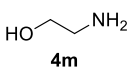
Table 2. Dehydrogenative Oxidation of Amines to Nitriles[a]



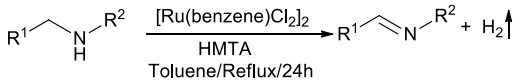
S.No.	Substrate	Product	% Yield [b]
1.	 4a	 5a	88
2.	 4b	 5b	91
3.	 4c	 5c	94
4.	 4d	 5d	86
5.	 4e	 5e	82
6.	 4f	 5f	81
7.	 4g	 5g	76
8.	 4h	 5h	75
9.	 4i	 5i	71
10.	 4j	 5j	83
11.	 4k	 5k	77
12.	 4l	 5l	79
13.	 4m	--	--

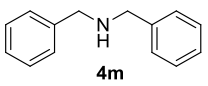
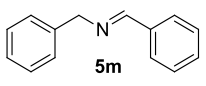
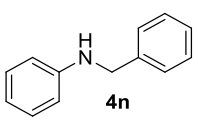
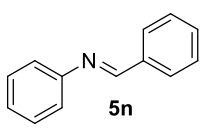
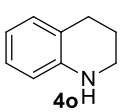
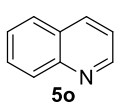
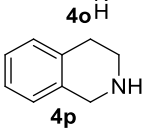
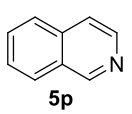
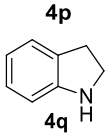
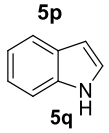
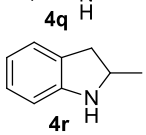
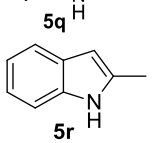
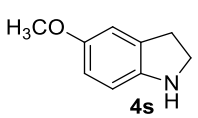
[a]Reaction conditions: reactions were carried out with amine substrate (0.5 mmol), $[Ru(benzene)Cl_2]_2$ (2 mol %), and HMTA (2 mol %) in toluene (1 mL) under reflux. [b]Isolated yields and average of at least two runs.

product, suggesting not only the highly chemoselective nature of the catalyst system but also the advantage of using a dehydrogenative oxidation method over an aerobic oxidation method. The presence of ortho substituents such as methyl (**4h**) and chloro (**4i**) groups resulted in decreased yields of the products **5h**,**i**, respectively (entries 8 and 9), suggesting that the developed catalyst system is sensitive to steric effects. In addition to arylamines a few alkylamines were also tested, and all of them gave the corresponding nitrile products in very good yields (entries 10−12). An attempt to oxidize 2-aminoethanol (**4m**) did not result in the formation of a nitrile product, leaving only unreacted starting material (entry 13).

Encouraged by results obtained from the double dehydrogenation of primary amines, we also tested the activity of the developed catalyst system for the oxidation of secondary amines and nitrogen-containing heterocyclic compounds. Dehydrogenation of several secondary amines including acyclic and cyclic amines (azaheterocycles) was tested, which afforded the corresponding dehydrogenated products, i.e. imines and enamines, in moderate to excellent yields, as depicted in Table 3. It has already been proved in the literature that inclusion of

Table 3. Dehydrogenative Oxidation of Secondary Amines[a]



S.No.	Substrate	Product	% Isolated Yield [b]
1.	 4m	 5m	79
2.	 4n	 5n	73
3.	 4o	 5o	84
4.	 4p	 5p	85
5.	 4q	 5q	87
6.	 4r	 5r	88
7.	 4s	5s	86

[a]Reaction conditions: reactions were carried out with amine substrate (0.5 mmol), $[Ru(benzene)Cl_2]_2$ (2 mol %), and HMTA (2 mol %) in toluene (1 mL) under reflux. [b]Isolated yields and average of at least two runs of the reaction.

nitrogen into a cyclic system facilitates the dehydrogenation process by decreasing the endothermicity of the reaction and thus these species are also considered as potential hydrogen storage materials/liquid hydrogen storage media.[19]

Dehydrogenation of dibenzylamine (**4m**) and *N*-benzylaniline (**4n**) resulted in very good yields of their corresponding imine products **5m**,**n**, respectively (Table 3, entries 1 and 2). Dehydrogenation of 1,2,3,4-tetrahydroquinoline (**4o**) and 1,2,3,4-tetrahydroisoquinoline (**4p**) proceeded to yield quino-

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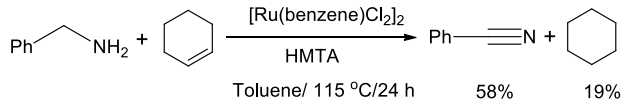
line (**5o**) and isoquinoline (**5p**), respectively, in very good yields (entries 3 and 4). Interestingly, both 1,2,3,4-tetrahydroquinoline and 1,2,3,4-tetrahydroisoquinoline resulted in exclusive formation of fully dehydrogenated products without forming any partially dehydrogenated products, which proves the high effeciency and selectivity of our catalyst system. Dehydrogenation of indoline (**4q**) was tested and resulted in the formation of indole (**5q**) in excellent yield (entry 5). Following this, 2-methylindoline (**4r**) was tested and resulted in the dehydrogenated product 2-methyl-1*H*-indole (**5r**) in excellent yield, which suggests that the catalyst system is not sensitive to steric effects (entry 6). Dehydrogenation of 5-methoxyindoline (**4s**) using our catalyst system also resulted in a very good yield of the dehydrogenated product **5s** (entry 7).

In order to identify the reaction pathway, the oxidation of benzylamine (**4a**) was carried out in the presence of cyclohexene as a hydrogen acceptor. In a typical closed-vessel reaction, benzylamine and cyclohexene in a 1:10 equiv ratio in dry and degassed toluene in the presence of **1** (2 mol %) and **2** (2 mol %) were heated at 115 °C for 24 h (Scheme 1). This

Scheme 1. Oxidation of Benzylamine (4a) in the Presence of Cyclohexene



resulted in the formation of cyclohexane in 19% yield (64% of conversion yield), which suggested that the reaction involved hydrogen evolution and followed a dehydrogenative pathway.

To investigate the role of HMTA (**2**) and the nature of the active catalyst, a series of NMR studies were carried out, as shown in Figure 2. An NMR-tube reaction of a solution of **1** and **2** in a 1:1 equiv ratio in DMSO-d_6 at room temperature showed major peaks corresponding to unreacted starting materials **1** and **2** in addition to slight formation of HMTA-coordinated ruthenium species at 4.46, 4.88, and 5.82 ppm (Figure 2A). When the reaction mixture was heated at 90 °C for 1 h in the NMR tube, in addition to the coordinated

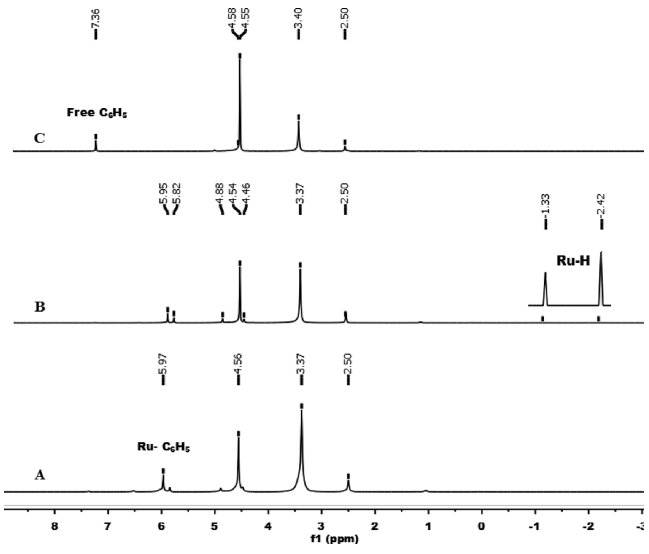


Figure 2. ^{1}H NMR evidence for the formation of ruthenium hydride intermediate.

HMTA ligand, two hydride signals were also observed at −1.33 and −2.42 ppm (Figure 2B). Continuing the heating further led to the elimination of both hydrogen and benzene from the active catalyst (Figure 2C). At high temperature free HMTA (**2**) as well as metal-coordinated HMTA complexes were reported to decompose to afford products such as NH_3, H_2, HCN, CH_4, and many others.[20a,d,e] It is also evident from the literature that the hydrogen byproduct which is formed from decomposition of **2** may act as the potential source of a hydride group.[20b,c] The observation of a hydride peak in the NMR spectra indicated that HMTA (**2**) can act as a source of a hydride group. Further, to support our claim of HMTA acting as a hydride donor, we performed another NMR study by heating a mixture of $RuCl_3 \cdot nH_2O$ and HMTA (**2**) in DMSO-d_6, which also resulted in a set of hydride peaks at −0.23 and −0.75 ppm (Figure S21).

In order to get an insight into the mechanism, the in situ ^{1}H NMR spectra of a mixture of **1** and **2** (Figure 2B) was compared with those of arene ruthenium hydride complexes available in the literature. Süss-Fink and co-workers reported a series of cationic trinuclear ruthenium hydride complexes obtained from the reaction of **1** with hydrogen in the presence of reagents such as $NaClO_4$, $NaBF_4$, NaCl, etc.[21] It was observed that the chemical shift values of hydride peaks obtained from our catalyst system were considerably shifted downfield in comparison to the hydride peak of −13.35 ppm reported for the cationic trinuclear species $[Ru(\eta^6\text{-}C_6H_6)(\mu\text{-}Cl)(\mu_3\text{-}O)(\mu\text{-}H)_2]^+$, which was obtained from a reaction of **1**, H_2, and $NaClO_4$.[21b] Further, the observed chemical shift values were found to be in good agreement with the values obtained for mononuclear Ru hydride species formed in situ from a reaction of $RuCl_3 \cdot nH_2O$ and **2** (Figure S21). These observations revealed that the skeletal formula of the active catalyst might be $[Ru(H)_2(C_6H_6)]$, and further investigations are underway to identify the exact structure and mechanism for its formation.

On the basis of the above experimental studies and literature reports[13a,22] the following mechanism is proposed for the double dehydrogenation of amines (Figure 3). According to the proposed mechanism, the active catalyst $[Ru(benzene)(H)_2]$ (**A**) generated from the reaction between **1** and **2** undergoes oxidative addition with an amine, followed by hydrogen elimination to form Ru−H intermediate **B**. Compound **B** undergoes β-hydrogen transfer to form imine-coordinated ruthenium complex **C**. The formation of an

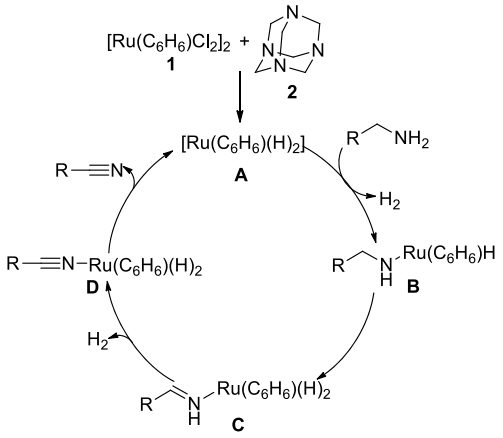


Figure 3. Mechanism involving double dehydrogenation of amine.

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ruthenium imine complex as an intermediate during the course of reaction was confirmed with the help of ^{1}H NMR (Figure S20) and was in agreement with a literature report.[22] The formation of a ruthenium imine complex as an intermediate during the double dehydrogenation of amine is different from that of the ruthenium imide complex reported by Szymczak and co-workers.[13a] Intermediate **C** undergoes β-hydrogen transfer with the elimination of hydrogen to the form nitrile-coordinated intermediate **D**. Compound **D** further undergoes reductive elimination to eliminate the nitrile product and regenerate the active catalyst **A**.

In conclusion, we have developed a very efficient in situ catalyst system using commercially available ruthenium(II) benzene dichloride dimer complex and hexamethylenetetramine for the acceptorless dehydrogenation of both primary and secondary amines. Mechanistic studies revealed the formation of a [Ru(benzene)$(H)_2$] fragment as the catalytically active species, while the oxidation of amines proceeded through a dehydrogenative pathway with the evolution of hydrogen gas. We have also experimentally shown the role of hexamethylenetetramine as a hydride donor in the above process.

EXPERIMENTAL SECTION

General Information. All procedures were carried out under purified nitrogen environment using standard Schlenk apparatus. All of the apparatus were oven-dried prior to use. An airless procedure was followed for all syntheses irrespective of the air stability of the final compounds. All of the solvents were used after a drying and degassing process. Other chemicals were purchased from commercial suppliers and used as received without further purification.

General Procedure for Dehydrogenation of Amine. [Ru(benzene)Cl_2]$_2$ (2 mol %), HMTA (2 mol %), amine, and dry toluene (1.0 mL) were placed in a Schlenk tube. The reaction mixture was stirred under open conditions to nitrogen and refluxed for 24 h. After completion of the reaction all of the toluene was evaporated under vacuum; the nitrile product was isolated from the crude mixture by column chromatography using hexane/EtOAc as eluent. The formation of the product was confirmed by comparing the ^{1}H NMR data with literature reports.

Procedure for Dehydrogenation of Benzylamine in the Presence of Cyclohexene. In a 50 mL closed-vessel reactor were placed [Ru(benzene)Cl_2]$_2$ (2 mol %), HMTA (2 mol %), benzylamine (0.05 mL, 0.5 mmol), cyclohexene (0.4 mL, 5 mmol), and dry toluene (0.6 mL). The resulting mixture was heated at 110 °C for 24 h. After completion of the reaction, the solution was cooled to room temperature and the yields were determined using gas chromatography.

*Benzonitrile (**5a**).*[23a] Colorless oil. Yield: 0.2196 g, 91%. The desired pure product was obtained after short silica gel column chromatography (hexane/ethyl acetate). ^{1}H NMR: δ 7.57−7.59 (m, 3H) and 7.41−7.44 (m, 2H) ppm.

*4-Methylbenzonitrile (**5b**).*[23d] Colorless oil. Yield: 0.2096 g, 90%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50 (d, J = 9 Hz, 2 H), 7.24 (d, J = 9 Hz, 2 H), 2.39 (s, 3 H) ppm.

*4-Methoxybenzonitrile (**5c**):*[23a] Colorless oil. Yield: 0.2253 g, 93%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37(d, J = 9 Hz, 2H), 6.78(d, J = 9 Hz, 2H), 3.79 (s, 3H) ppm.

*4-Chlorobenzonitrile (**5d**).*[23c] White solid. Yield: 0.2065 g, 85%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (d, J = 9 Hz, 2 H), 7.52 (d, J = 9 Hz, 2 H) ppm.

*4-Fluorobenzonitrile (**5e**).*[23b] Colorless oil. Yield: 0.2002 g, 83%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.85 (d, J = 9 Hz, 2 H), 7.37 (d, J = 9 Hz, 2 H) ppm.

*4-Nitrobenzonitrile (**5f**).*[23c] White solid. Yield: 0.1863 g, 77%. The desired pure product was obtained after short column chromatography, hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.18 (d, J = 9 Hz, 2 H), 7.52 (d, J = 9 Hz, 2H) ppm.

*4-Aminobenzonitrile (**5g**).*[23a] Pale yellow solid. Yield: 0.1023 g, 42%. The desired pure product was obtained after short column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ= 7.42 (d, J = 9 Hz, 2 H), 6.64 (d, J = 6 Hz, 2H), 4.16(s, 2H) ppm.

*2-Methylbenzonitrile (**5h**).*[23d] Colorless oil. Yield: 0.1521 g, 63%. The desired pure product was obtained after short column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ= 7.56−7.58 (m, 1H), 7.46−7.48 (m, 1H), 7.28−7.32 (m, 2H), 2.53 (s, 3H) ppm.

*2-Chlorobenzonitrile (**5i**).*[23e] Colorless oil. Yield: 0.1421g, 58%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ= 8.33−8.35 (m, 1 H), 7.58−7.63 (m, 1H), 7.26−7.29 (m, 1H), 7.16−7.20 (m, 1H) ppm.

*2-Phenylacetonitrile (**5j**).*[23h] Colorless liquid. Yield: 0.2002 g, 82%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate).^{1}H NMR ($CDCl_3$, 300 MHz): δ= 7.32−7.40 (m, 5H), 3.70 (s, 2H) ppm.

*1-Heptanenitrile (**5k**).*[23g] Colorless liquid. Yield: 0.1832 g, 72%.The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate).^{1}H NMR ($CDCl_3$, 300 MHz): δ= 2.34 (t, J = 6 Hz, 2H), 1.66 (q, J = 6 Hz, 2H), 1.45−1.57 (m, 2H), 1.32 (bs, 4H), 0.90 (t, J = 3 Hz, 3H) ppm.

*Octanenitrile (**5l**).*[23g] Colorless liquid. Yield: 0.1913 g, 79%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.34 (t, J = 6 Hz, 2H), 1.66(p, J = 6 Hz, 2H), 1.45 (m, 2H), 1.30(bs, 6H), 0.89 (t, J = 3 Hz, 3H) ppm.

*N-Benzylidene-1-phenylmethanamine (**5m**).*[23f] Colorless liquid. Yield: 0.1954 g, 79%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.44 (s, 1H), 7.85−7.87 (m, 1H), 7.48 (bs, 2H), 7.47 (bs, 2H), 7.42 (bs, 2H), 7.40−7.41 (m, 2H), 7.32−7.35 (m, 1H), 4.88 (s, 2H) ppm.

*N-Benzylideneaniline (**5n**).*[23f] Colorless liquid. Yield: 0.1804g, 73%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.44 (s, 1H), 7.89 (t, J = 3 Hz, 2H), 7.45−7.47 (m, 2H), 7.36−7.39 (m, 1H), 7.23−7.25 (m, 2H), 7.21−7.22 (m, 2H), 7.19−7.20 (m, 1H), ppm.

*Quinoline (**5o**).*[24] Colorless liquid. Yield: 0.2036 g, 84%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.92 (t, J = 6 Hz, 1 H), 8.14−8.17 (m, 1H), 8.10−8.13 (m, 1H), 7.80−7.83 (m, 1 H), 7.69−7.74 (m, 1 H), 7.51−7.57 (m, 1H), 7.37−7.41 (m, 1H) ppm.

*Isoquinoline (**5p**).*[24] Yellow liquid. Yield: 0.2088 g, 85%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.24 (s, 1H), 8.51 (d, J = 6 Hz, 1 H), 7.94 (d, J = 12 Hz, 1 H), 7.79 (d, J = 6 Hz, 1 H), 7.68−7.70 (m, 1 H), 7.61−7.64 (m, 1 H).7.55−7.58 (m, 1H) ppm.

*Indole (**5q**).*[24] White solid. Yield: 0.2137 g, 87%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.12 (s, 1 H), 7.21−7.24 (m, 5H), 6.59−6.60 (m, 1 H).

*2-Methyl-1H-indole (**5r**).*[24] Yellow solid. Yield: 0.2183 g, 89%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87 (s, 1 H), 7.62−7.60 (m, 1 H), 7.38−7.35 (m, 1 H), 7.14−7.22 (m, 2 H), 6.98−6.99 (m, 1 H), 2.36 (s, 3 H) ppm.

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*5-Methoxyindole (**5s**).*[24] White solid. Yield: 0.2120 g, 86%. The desired pure product was obtained after short-column chromatography (hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.08 (s, 1 H), 7.28 (d, J = 9 Hz, 1 H), 7.15−7.19 (m, 2H), 6.93 (m, 1H), 6.52 (s, 1 H), 3.89 (s, 3 H) ppm.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00399.

NMR spectra of oxidation products (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This work is dedicated to Professor Anil J. Elias on the occasion of his 58th birthday.

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