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Oxidant-Free Conversion of Primary Amines to Nitriles

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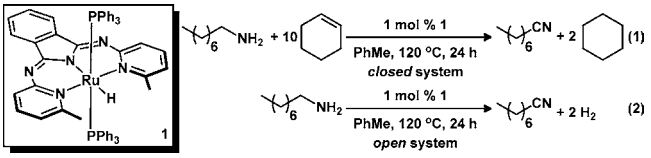
Supporting Information

ABSTRACT: An amide-derived NNN-Ru(II) hydride complex catalyzes oxidant-free, acceptorless, and chemoselective dehydrogenation of primary and secondary amines to the corresponding nitriles and imines with liberation of dihydrogen. The catalyst system tolerates oxidizable functionality and is selective for the dehydrogenation of primary amines ($-CH_2NH_2$) in the presence of amines without α-CH hydrogens.

Nitriles are a prominent class of organic molecules included in a wide variety of natural products,[1] biologically active compounds,[2] and industrial processes (polymers, agrochemicals, and dyes/pigments)[3] and used as synthons for further synthetic elaboration.[4] Typical routes to prepare nitriles proceed with low atom economy, require toxic reagents, and/or have limited selectivity. Common laboratory-scale syntheses include Sandmeyer-type reactivity,[5] cyanation of alkyl or aryl halides,[6] dehydration of amides/aldoximes,[7] and metal-catalyzed cyanation/cyanomethylation,[8] among others.[9] In contrast, industrial syntheses typically rely on ammoxidation protocols that operate at high temperatures (300−550 °C).[3,10] All of the above synthetic methodologies require either the use of hazardous/energy-intensive reagents, harsh reaction conditions, and/or produce stoichiometric waste. Moreover, reagents and conditions required for these transformations often show limited compatibility with other functional groups. Another methodology for nitrile synthesis that does not introduce a carbon unit is the oxidation of primary amines,[11] which can be mediated using stoichiometric inorganic[12] or iodine-based oxidants[13] or a transition-metal catalyst and O_2.[14] Unfortunately, many transition-metal catalyzed oxidation protocols require excess quantities of oxidant and/or basic reagent for efficient catalysis, which decreases atom economy by contributing to unwanted waste products.[11b,13b,c,14a,b] Furthermore, the use of an external oxidant limits selectivity and functional group tolerance, because oxidant-incompatible functionality must then be protected prior to the nitrile formation step.[14]

An alternative procedure for amine oxidation is to use transition-metal catalyzed dehydrogenation, which has been widely exploited for alcohol oxidation.[15] However, reports detailing oxidant-free amine dehydrogenation are limited and either proceed with low conversion[16] or require exogenous additives and harsh reaction conditions (160−200 °C).[17] Our laboratory recently reported base-free, acceptorless, and chemoselective dehydrogenation and dehydrogenative coupling reactions of secondary and primary alcohols/diols, respectively, catalyzed by an amide-derived NNN-Ru(II) hydride complex (**1**, $HRu(bmpi)(PPh_3)_2$; bmpi =1,3-bis(6′methyl-2′-pyridylimino)isoindoline).[18] Because of the ability of **1** to promote rapid H_2 release from alcohol groups without product inhibition, we surmised that **1** might also dehydrogenate other polar substrates by a similar mechanistic pathway. Herein, we report the application of **1** as a catalyst that efficiently promotes dehydrogenation of primary and secondary amines to nitriles and imines, respectively, without the requirement of exogenous oxidant or hydrogen acceptor.

In contrast to the growing number of reports detailing catalytic dehydrogenation of alcohols, analogous dehydrogenative reactivity of amines is sparse[15f,19] and even less reported for the double dehydrogenation to afford the corresponding nitrile.[16,17] Moreover, one of the only well-defined examples of direct amine dehydrogenation employed an olefin as a hydrogen acceptor[17a] or excess base[17b] to drive the reaction at high temperatures (160−200 °C).[17] In light of this precedent, we initiated investigations by examining transfer dehydrogenation of *n*-octylamine with cyclohexene catalyzed by **1**. When a toluene solution containing 0.5 mmol *n*-octylamine, 5 mmol (10 equiv) of cyclohexene and 1 mol % of **1** was heated to 110 °C for 24 h in a sealed vessel, *n*-octanenitrile was observed (40%) with concomitant formation of cyclohexane, as determined by GC-MS analysis (eq 1).



Under these conditions, the added hydrogen acceptor (cyclohexene) was critical to promote the reaction, and in the absence of a hydrogen acceptor (3.5 mL headspace), less than 4% conversion to *n*-octanenitrile was observed. The conversion efficiency was found to be sensitive to the overall reaction volume (liquid plus headspace), consistent with a reaction in which a gas is generated. In the limiting regime of an infinitely large headspace (i.e., an open system), the efficiency of **1** was further improved. For example, in the presence of **1** (1 mol %),[20] *n*-octylamine was converted to *n*-octanenitrile in 76% yield after heating for 24 h in refluxing toluene open to a N_2 atmosphere (eq 2). H_2 and *n*-octanenitrile were confirmed as the sole reaction products by *in situ* examination of the reaction mixture in a sealed NMR tube and control experiments showed no reaction in the absence of **1** (Supporting Information).

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In order to evaluate the extent to which the release of H_2 mediates the dehydrogenation reaction, we assessed the product profile under elevated H_2 pressures (Figure 1).

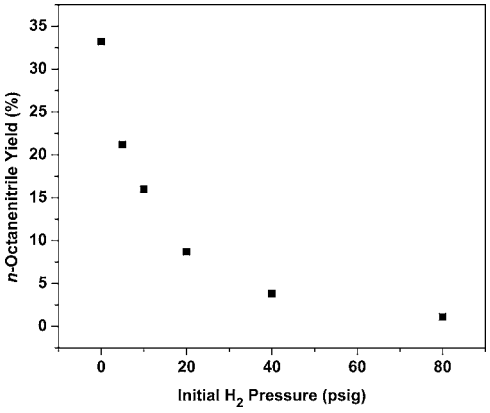


Figure 1. Dependence of *n*-octylamine dehydrogenation catalyzed by **1** on the initial H_2 pressure. Conditions: *n*-octylamine (0.5 mmol), **1** (1 mol %), and toluene (0.5 mL) were charged with H_2 in a Fisher-Porter tube (85 mL) and heated to 110 °C for 24 h.

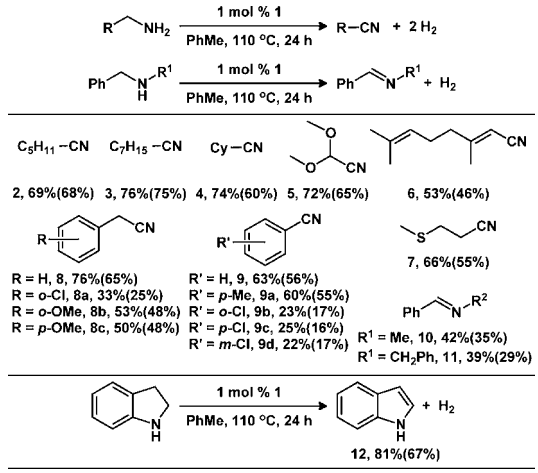
Consistent with prior dehydrogenative alcohol oxidation studies,[18] the conversion efficiency of the reaction was found to be highly sensitive to pressure and the dehydrogenation reaction was significantly suppressed (33% yield) when performed in a sealed Fischer–Porter tube (84.5 mL headspace). The conversion decreased with increased H_2 pressure: halving at 10, 20, 40, and 80 psig.

Dehydrogenation of aliphatic amines was general to afford the corresponding nitriles as the exclusive product (**2**–**7**). For instance, when 1-cyclohexylmethanamine was used as a substrate, cyclohexanecarbonitrile (**4**) was generated in 74% yield. Furthermore, the dehydrogenation of 2-phenethylamine to 2-phenylacetonitrile (**8**), an important precursor to several pharmaceutical drugs,[3] proceeded with 76% yield. When *ortho*- and *para*-substituted phenethylamines were used as substrates, conversions to the corresponding phenylacetonitriles depended on the electron-donating and -withdrawing groups on the benzene ring (**8a**–**c**). A modest (33%) yield was observed for the *ortho*-substituted chlorophenethylamine, however, replacing the chloro group for an electron-donating methoxy substituent increased the yield to 53%. The proximity of the methoxy substituent to the $-CH_2NH_2$ group had little effect on the conversion efficiency, since both the *ortho*- and *para*-substituted methoxyphenethylamines gave similar yields.

Dehydrogenation reactions of activated amines were investigated with benzylic substrates, which were cleanly converted to the corresponding benzonitriles. Substituent effects were examined using a series of functionalized benzylamines. While electron-donating groups were tolerated (**9a**), electron-withdrawing groups decreased the yields, regardless of the substitution pattern on the aromatic ring. For instance, deactivating chloro groups at either the *ortho*-, *meta*-, or *para*-positions led to decreased conversions (**9b**–**d**).

Because we observed high selectivity for primary amines, we investigated whether **1** could also catalyze the selective dehydrogenation of secondary amines. Oxidative protocols for primary and secondary amines have been reported using O_2; however, selectivity is generally low with this methodology.[14] For example, oxidation of secondary amines affords mixtures of products that include aldehydes and alcohols in addition to nitrogen-containing species.[14e–h] In contrast, a single product was obtained from the dehydrogenation of secondary and heterocyclic amines with $-CH_2NRH$ functionalities catalyzed by **1**. In the case of secondary amines, secondary aldimines (**10**,**11**) were obtained in moderate yields, and indoline was cleanly converted to indole (**12**) in high (81%) yield. Thus, in addition to primary amine oxidation, **1** exhibits high selectivity for the catalytic dehydrogenation of secondary and select heterocyclic amines.

Table 1. Dehydrogenation of Amines Catalyzed by 1[a]



[a]Reactions performed on 0.5 mmol scale. Yields were determined by GC-MS using *n*-docosane as an internal standard. Isolated yields are reported in parentheses.

In contrast to (transfer) dehydrogenation reactivity of alcohols,[15h,21] reports of analogous reactivity with amines are limited.[16,17] Consistent with the lack of literature precedent, we observed only trace (1–3%) nitrile formation from *n*-octylamine using several common transfer hydrogenation catalysts (Noyori's $HRuCl(PPh_3)_2(en)$ catalyst,[22] $Ru(H)_2(PPh_3)_4$,[23] $HRuCl(PPh_3)_3$,[24] and $HRuCl(PPh_3)_3CO$[25]). Similar results (less than 1% *n*-octanenitrile) were obtained when $HRh(P^iPr_3)_3$ and *n*-octylamine were subjected to identical condition as for the dehydrogenation by **1**.[26] Shvo's catalyst[27] exhibited a reaction profile consistent with amine coupling, affording dioctylamine in 22% yield after 24 h with no conversion to *n*-octanenitrile.[28] Based on known reports as well as our own comparative experiments, the double dehydrogenation reactivity mediated by **1** is atypical in terms of conversion and product selectivity.

The oxidation of amines to nitriles without any required additives allows our system to tolerate potentially oxidizable functional groups; a limitation of traditional amine to nitrile conversions. To highlight the utility of the amine oxidation under the reducing conditions used by **1**, we examined primary amine dehydrogenation in the presence of a thioether functionality, a motif typically susceptible to oxidation.[29] Indeed, when 3-(methylthio)propylamine was subjected to **1**, only the amino moiety was oxidized under the standard reaction conditions and 3-(methylthio)propanenitrile (**7**) was obtained as the single product, produced in 66% yield. This reactivity demonstrates the utility of **1** as an amine oxidation catalyst that is compatible with an oxidant intolerant functionality.

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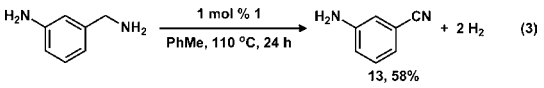
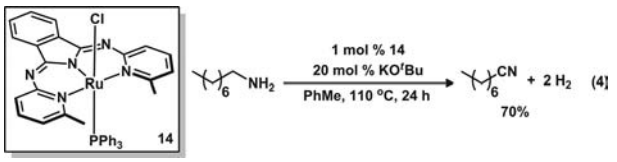
The preparation of aryl nitriles is typically achieved using Sandmeyer-type[5] or Rosenmund−von Braun[6] methodologies, but conditions necessary to promote these transformations also limit chemoselectivity. Because α-CH hydrogens are required to eliminate H_2, an amine double dehydrogenative methodology allows the differentiation of a substrate containing two chemically distinct amino functional groups ($-CH_2NH_2$ vs $-CR_2NH_2$). To highlight this difference, complex **1** selectively oxidized the benzyl amine moiety of 3-aminobenzylamine in the presence of the aromatic amino group, which afforded 3-aminobenzonitrile (**13**) as the sole product in 58% yield (54% isolated yield), demonstrating the high chemoselectivity of **1** (eq 3). Furthermore, this illustrates the utility of dehydrogenative oxidation reactions mediated by **1**; instead of requiring an oxidant, amine oxidation is achieved by H_2 elimination.



Catalytic dehydrogenation reactions can be mediated by either heterogeneous or homogeneous pathways, and the catalytically active form of **1** was initially probed using catalyst poisoning studies.[30] Consistent with an operative homogeneous system, the catalytic activity of *n*-octanenitrile formation was unaffected by the addition of Hg(0) (~800 equiv) when added during catalysis. A substoichiometric ligand poisoning experiment was conducted to further interrogate the active catalytic species.[31] In the presence of 0.25 equiv 1,10-phenanthroline, no change in the product distribution was noted, however, complete poisoning was achieved using 1 equiv 1,10-phenanthroline, inconsistent with a heterogeneous system, where low surface area aggregates are typically poisoned by ≪1 equiv added ligand poison.[32]

Further investigations into the identity of catalytically active species are currently underway, and preliminary analyses suggest a catalytic cycle similar to alcohol dehydrogenation.[15h] *In situ* analysis of the amine dehydrogenation reaction revealed the release of PPh_3 from **1** during catalysis, as visualized by ^{31}P NMR spectroscopy and GC-MS analysis. Furthermore, catalytic reactions using Ru(bmpi)(PPh_3)Cl (**14**) exhibited a similar dehydrogenation profile to **1** in the presence of KO^{t}Bu (eq 4),



and free PPh_3 was not observed. This is consistent with a single PPh_3 dissociation event from **1** to generate a catalytically active 16 e^- Ru^{II} species, able to participate in an inner-sphere type dehydrogenation pathway.[33]

When the dehydrogenation of *n*-octylamine was monitored *in situ* by GC-MS and ^1H NMR spectroscopy over 24 h in an open system,[34] unreacted *n*-octylamine and *n*-octanenitrile were the only species observed. Because neither imine nor imine-derived products were detected, a fast secondary dehydrogenation event is proposed to yield the nitrile product.[35] Since nitriles are competent ligands for transition metals, nitrile coordination might be an operative inhibition pathway at high nitrile concentrations. To probe this possibility, the dehydrogenation of *n*-octylamine was performed in the presence of *n*-octanenitrile (50 equiv).[36] Under the standard reaction conditions, 54% conversion was noted, consistent with competitive binding of nitrile to the catalytically active Ru species. This trend continued at 75 equiv *n*-octanenitrile, where only 12% conversion was noted. These results are consistent with catalyst inhibition at high concentrations of nitrile, where competitive nitrile-coordination diverts the catalyst from a productive dehydrogenation pathway. Hence, we propose that following amine coordination, H_2 loss affords an imine intermediate that remains coordinated to Ru. This species likely undergoes a further fast dehydrogenation reaction to afford a Ru-nitrile adduct that is substitutionally labile at low nitrile concentrations, but inert at high nitrile concentrations.

In conclusion, we have developed a selective dehydrogenative amine oxidation protocol that requires no oxidant or hydrogen acceptor additives, tolerates oxidizable functionality, and liberates H_2 as a product. Although, prior reports demonstrated oxidative reactivity of primary amines to nitriles, our system is the only reported homogeneous catalyst to accomplish this without any additives and in good yields. Additionally, the amine dehydrogenation methodology is notable because **1** mediates the chemoselective oxidation of primary amines with $-CH_2NH_2$ functionality in the presence of primary amines without α-CH hydrogens. Further work is ongoing to clearly elucidate the mechanism of amine dehydrogenation and to examine its utility for energy-relevant transformations, including the possibility of using amines as reversible liquid H_2 carriers,[37] where selective amine dehydrogenation is a required.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(20) When 5 mol % of **1** was used, *n*-octylamine was converted to *n*-octanenitrile in 80% yield (see Table S1 and Figure S1). While this small increase in conversion was noted with higher catalyst loadings, our standard reaction conditions employed 1 mol %.
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(28) Note that this complex was previously reported to promote amine coupling to generate secondary amines. The proposed pathway operates via a hydrogen borrowing mechanism where imine dissociation occurs after amine dehydrogenation. The free imine is susceptible to nucleophilic attack by an amine, followed by ammonia elimination. See (a) Conley, B. L.; Pennington-Boggio, M. K.; Boz, E.; Williams, T. J. *Chem. Rev.* **2010**, *110*, 2294. (b) Hollmann, D.; Haijun, J.; Spannerberg, A.; Bahn, S.; Tillack, A.; Parton, R.; Altink, R.; Beller, M. *Organometallics* **2009**, *28*, 473. (c) Jung, C. W.; Fellmann, J. D.; Garrou, P. E. *Organometallics* **1983**, *2*, 1042.
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(32) Water also acts as a catalyst poison. For instance, in the presence of 0.25 equiv H_2O, 42% yield of *n*-octanenitrile was noted. Accordingly, the reproducibility of catalysis was highly susceptible to water content. All amines were subjected to an identical protocol for drying (see Supporting Information), and highly reproducible yields were obtained.
(33) Attempts to elucidate the catalytic species under stoichiometric amine or nitrile conditions were complicated by the presence of paramagnetic species that were generated during the reaction.
(34) See Figure S2 for the reaction profile of *n*-octylamine dehydrogenation catalyzed by **1**. Although 65% conversion was noted within 6 h for *n*-octylamine, 24 h was used for all amine substrates to ensure maximum conversion.
(35) Note that primary aldimines are unstable under our reaction conditions, see reference: Lee, J. H.; Gupta, S.; Jeong, W.; Rhee, Y. H.; Park, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 10851.
(36) A large excess of *n*-octanenitrile was used to replicate the nitrile concentration under standard reaction conditions. Note that using 1 or 2 equiv *n*-octanenitrile did not affect the overall yield.
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