Efficient Ruthenium-Catalyzed Aerobic Oxidation of Amines by Using a Biomimetic Coupled Catalytic System

Joseph S. M. Samec, Alida H. Éll, and Jan-E. Bäckvall*[a]

Abstract: Efficient aerobic oxidation of amines was developed by the use of a biomimetic coupled catalytic system involving a ruthenium-induced dehydrogenation. The principle for this aerobic oxidation is that the electron transfer from the amine to molecular oxygen occurs stepwise via coupled redox systems and this leads to a low-energy electron transfer. A substrate-selective ruthenium catalyst dehydrogenates the amine and the hydrogen atoms abstracted are transported to an electron-rich quinone (**2a**). The hydroquinone thus formed is subsequently reoxidized by air with the aid of an oxygen-activating [Co(salen)]-type complex (**27**). The reaction can be used for the preparation of ketimines and aldimines in good to high yields from the appropriate corresponding amines. The reaction proceeds with high selectivity, and the catalytic system tolerates air without being deactivated. The rate of the dehydrogenation was studied by using quinone **2a** as the terminal oxidant. A catalytic cycle in which the amine promotes the dissociation of the dimeric catalyst **1** is presented.

Keywords: homogeneous catalysis · imines · oxidation · ruthenium

Introduction

Oxidation reactions are of fundamental importance in organic chemistry.[1] Stoichiometric amounts of metal-based oxidants such as dichromate ions, permanganate ions, manganese dioxide, silver oxide, and lead tetraacetate are still used in many oxidations.[2] The stoichiometric use of such oxidants is undesirable from both an environmental and an economic point of view. Therefore much attention has been paid to the use of a transition-metal catalyst to achieve efficient oxidations with molecular oxygen or hydrogen peroxide as terminal oxidants.[1,2] One challenge to overcome when using a substrate-selective transition-metal catalyst is the usually high energy barrier for the reoxidation of the reduced form of the metal by molecular oxygen. An efficient and successful way to circumvent the high-energy pathway for reoxidation of the metal is to mimic biological oxidations, where large jumps in oxidation potentials are avoided by the use of several coupled redox catalysts as electron-transfer mediators (ETMs).[3] A number of such oxidation systems that mimic biological electron transfer are known.[4–11] In these so-called biomimetic oxidations the electrons are smoothly transported from the reduced form of the substrate-selective catalyst (often a transition metal) to molecular oxygen or hydrogen peroxide (Figure 1).

Our group has recently designed and developed coupled catalytic electron transfer systems for 1,4-oxidations of conjugated dienes,[4] allylic oxidations,[4a,5] oxidations of alcohols,[6] and dihydroxylations of olefins[7] for which either O_2 or H_2O_2 are used as the oxidant.

Imines are useful intermediates in organic synthesis, which act as electrophilic reagents in many different reactions such as reductions, additions, condensations, and cycloadditions (see Scheme 1 for some examples). Many of these transformations can be carried out with high enantioselectivity. Imines also occur as intermediates in the racemization of chiral amines.[12] The standard protocol for their synthesis involves condensation of an amine and a carbonyl compound (aldehyde or ketone). Owing to their unstable and reactive nature it would be desirable to obtain imines by pathways other than those from an electrophilic carbonyl compound. Amines are stable and easily accessible compounds and would therefore be suitable precursors for imines by dehydrogenation.

The biological oxidation of amines involves amine dehydrogenases/oxidases, which are important in a variety of processes ranging from bacterial growth on amines to the oxidation of neurotransmitters in animals.[20] The oxidation is initiated by a condensation of the amine to a quinone,

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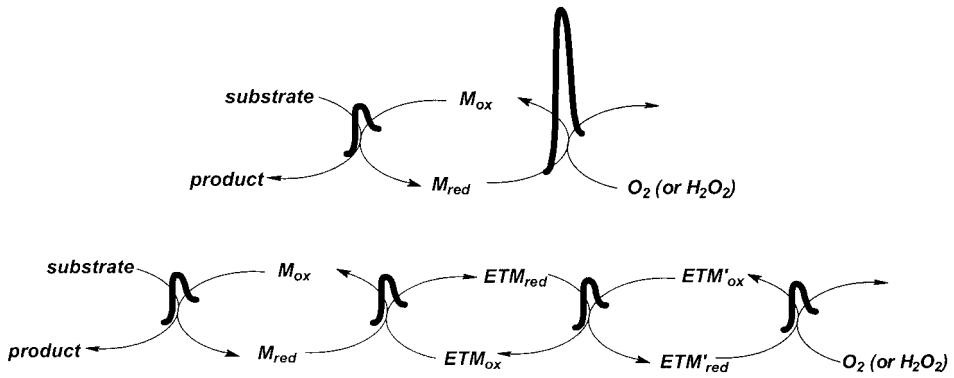
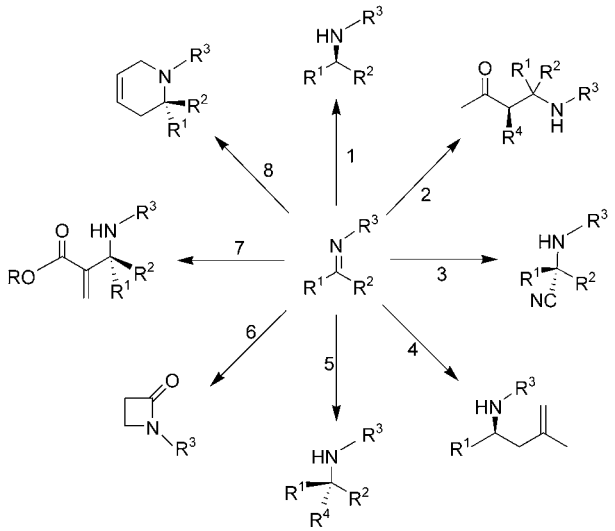


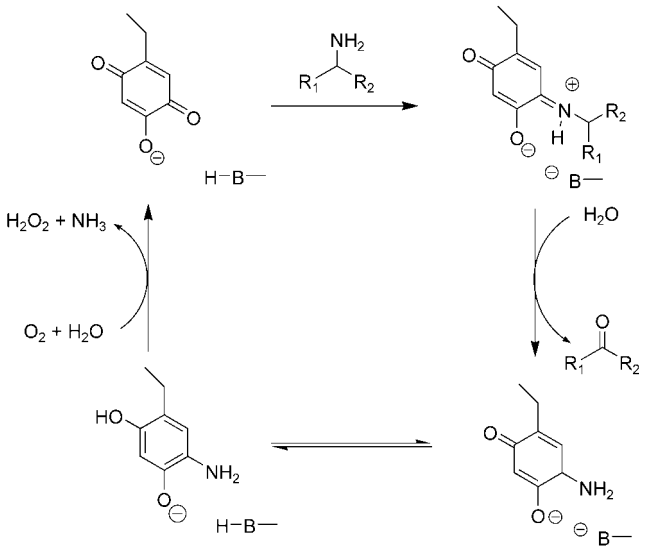
Figure 1. Dividing the oxidation potential using catalyst and ETM.



Scheme 1. Imines as important intermediates: 1) hydrogenation;[13] 2) Mannich;[14] 3) Strecker;[15] 4) imino—ene;[16] 5) addition; 6) [2 + 2] addition;[17] 7) aza-Baylis—Hillman;[18] 8) aza-Diels—Alder.[19]

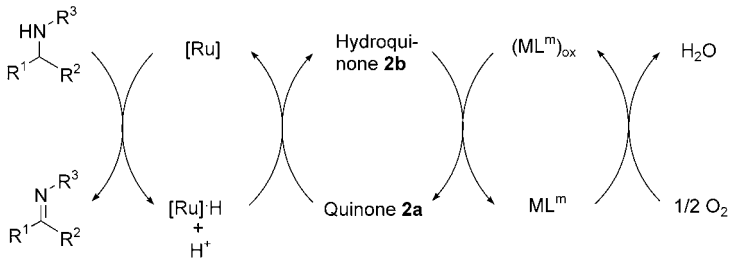
leading to the formation of an iminoquinone. Water hydrolysis of this intermediate releases the carbonyl compound. The aminoquinol is subsequently oxidized back to quinone by molecular oxygen, which releases ammonia (Scheme 2). The problem with mimicking these systems is that the amines are not dehydrogenated but rather react with a carbonyl group of a quinone, forming an imine intermediate that is hydrolyzed to a ketone. Therefore this is not a suitable path to mimic the generation of imines.

We therefore searched for alternative pathways for the aerobic oxidation of amines to imines. A few methods for the oxidation of amines to imine are known in the literature.[21] Murahashi et al.[22] reported a ruthenium-catalyzed oxidation using *t*BuOOH as the oxidant, and James and Bailey[23] described a porphyrin-catalyzed aerobic procedure for the oxidation of amines to imines.[24] We recently found that the coupled catalytic system involving the ruthenium complex **1** (see [Eq. (1)]) and 2,6-dimethoxy-1,4-benzoquinone (**2a**) as catalysts and MnO_2 as terminal oxidant efficiently promoted the dehydrogenation of aromatic amines to their corresponding ketimines.[25] Jensen and co-workers reported an iridium pincer complex that catalyzed the dehydrogenation of amines to the corresponding imines using an olefin as terminal oxidant.[26] However, very harsh reaction conditions were required for this transformation. Recently, Mizuno and co-workers reported a ruthenium-catalyzed heterogeneous aerobic oxidation of primary amines to nitriles.[27] This system also catalyzed the oxidation of secondary amines to aldimines and two examples were given. A



Scheme 2. Biological oxidation of amines.

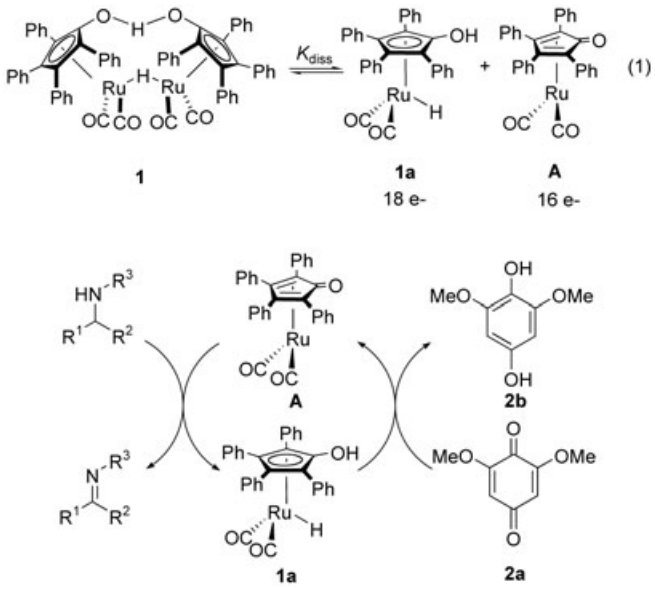
problem with the latter reaction is that overoxidation to nitrile occurs and therefore the selectivity to imine is moderate. The lack of mild catalytic procedures to obtain both ketimines and aldimines motivated further studies of the oxidation of amines. Here we describe a mild and efficient aerobic catalytic system for the generation of aldimines and ketimines by ruthenium-catalyzed dehydrogenation of amines involving a biomimetic coupled catalytic system. The design of the system was inspired by the biological oxidation of secondary alcohols. Instead of NAD^+ we employed a ruthenium complex as the substrate-selective catalyst, the ubiquinone (Q) was replaced by another electron-rich quinone (**2a**), and in place of cytochrome c, a metal macrocycle (ML^m), a [Co(salen)]-type complex, was used for the O_2 activation (Scheme 3).



Scheme 3.

Results and Discussion

Choice of catalyst: In a previous study we showed that catalyst **1** is efficient in catalyzing the dehydrogenation of aromatic amines to ketimines.[25] The rate-limiting step of this process is the transfer of the α-hydrogen atom from the substrate to ruthenium.[28] In the dehydrogenation of *N*-phenyl-1-phenylethylamine with the Shvo catalyst **1**, where the 16-electron complex **A** is the active catalyst, a deuterium isotope effect k_{CHNH}/k_{CDNH} of 3.24 compared to k_{CHNH}/k_{CDND} of 3.26 was observed.[28] The active species **A** is continuously regenerated from **1a** by reaction with the quinone **2a** (Scheme 4).

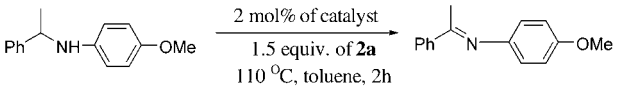


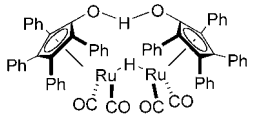
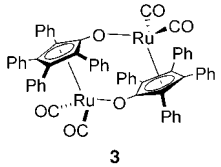
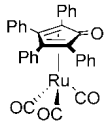
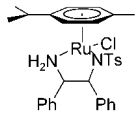
Scheme 4.

The active species **A** can be generated also from the dimeric structure $[\{Ph_4(\eta^5\text{-}C_4CO)Ru(CO)_2\}_2]$ (**3**) as recently reported by Casey and co-workers[29] or from $[\{Ph_4(\eta^4\text{-}C_4CO)\}Ru(CO)_3]$ (**4**) by loss of CO. We found that both complexes **1** and **3** showed a high activity in the transfer dehydrogenation of *N*-(4-methoxyphenyl)-*N*-(1-phenylethyl)-amine using 2,6-dimethoxy-1,4-benzoquinone (**2a**) as oxidant (entries 1 and 2, Table 1). However, complex **4** showed lower activity than catalysts **1** and **3** most likely due to the required CO dissociation from ruthenium being slow (entry 3, Table 1). Both Noyori's catalyst (**5**) and $[RuCl_2(PPh_3)_3]$ (**6**), which have been successfully used in the transfer hydrogenation of imines,[13,30] showed very low activity in the dehydrogenation (entries 4 and 5, Table 1).

Substrate effect on the rate: In the transfer hydrogenation of imines, we found that the rate of the reaction was dependent on the electronic properties of the substrate.[31] Thus, electron-rich substrates gave a higher rate (measured in TOF) than electron-deficient substrates. For example, when *N*-phenyl-(1-phenylethylidene)amine was substituted for *N*-phenyl-[1-(4-methoxyphenyl)ethylidene]amine the rate was increased from 730 to 840 h^{-1}, whereas a *p*-fluoro substituent in the same position decreased the rate from 730 to 120 h^{-1}.[31] Interestingly the same trend was found also for the dehydrogenation reaction using catalyst **3**, where the

Table 1. Catalyst screening.[a]

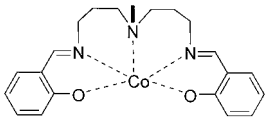


Entry	Catalyst	Yield [%] after 2 h[b]
1	 **1**	97
2	 **3**	95
3	 **4**	33
4	 **5**	10[c]
5	$[RuCl_2(PPh_3)_3]$ **6**	5[c]

[a] The reactions were carried out on a 0.125-mmol scale in toluene (1 mL) at 110 °C with 2 mol % of Ru catalyst and 1.5 equivalents of quinone **2a**. [b] Determined by ^1H NMR spectroscopy. [c] 4 mol % of K_2CO_3 was added.

rate of the reaction (calculated in TOF) was higher for electron-rich substrates. For example, substrates having a methoxy or a methyl group on one of the aromatic rings displayed higher rates (entries 1–6, Table 2). An additive effect was found when more than one methoxy group was introduced (entry 1, Table 2). In the transfer hydrogenation of imines, we observed that aldimines react slower than ketimines. We observe the same trend for the reversed reaction studied here, dehydrogenation of amines, that is, aldimines are generated slower than ketimines (entry 9, Table 2). In contrast to the transfer hydrogenation of imines, an ethyl group instead of a methyl group α to the amino function did not increase the rate (entry 8, Table 2). A possible explanation for the latter is that the dehydrogenation is more sensitive towards steric effects than transfer hydrogenation. A *p*-CN substituent on one of the phenyl rings made the amine unreactive under the general conditions used. However, a high TOF was obtained using microwave assistance (entry 10, Table 2).

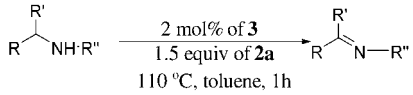
Aerobic oxidation of amines: To develop an aerobic process for the oxidation of amines to imines it is necessary to reoxidize the dimethoxyquinone **2** with molecular oxygen. For the alcohol oxidation in biological systems, ubiquinol is reoxidized to ubiquinone with molecular oxygen, which is activated by an iron porphyrin in cytochrome c.[32] Recently, we reported a successful coupled oxidation system of secondary alcohols that mimics this biological system where hydroquinone **2b** was reoxidized by O_2 to generate **2a**.[6c] In this system the [Co(salen)]-type complex **27** was found to be efficient for the activation of molecular oxygen and catalyzed the reoxidation of **2b** to **2a**. It was of interest to find out if this artificial oxidation system also could be applied to the aerobic oxidation of amines. One concern was that the water formed may hydrolyze the imine to give a ketone (aldehyde). Initial attempts to use the coupled aerobic system for oxidation of amines to imines gave varying results, and difficulties were encountered to obtain good yields. After some variation of the reaction conditions we found that a moderate stream of air through the reaction flask gave the best results.

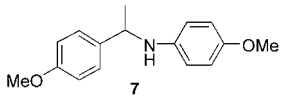
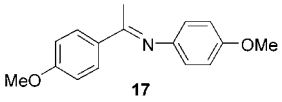
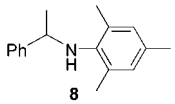
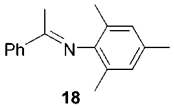
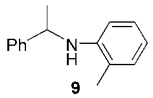
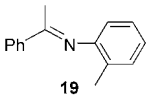
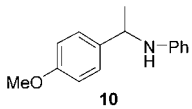
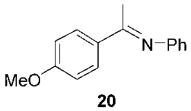
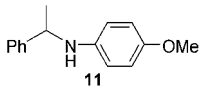
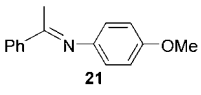
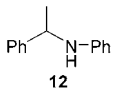
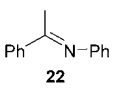
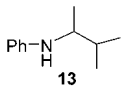
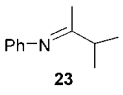
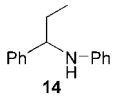
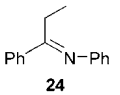
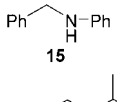
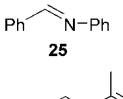
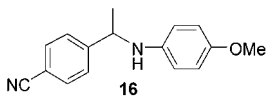
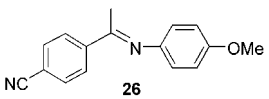


27

Thus, the biomimetic system used for alcohols[6c] works well also for the dehydrogenation of amines to imines in good to

Table 2. Ruthenium-catalyzed dehydrogenation of amines to imines by quinone **2a**.[a]

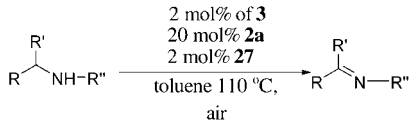


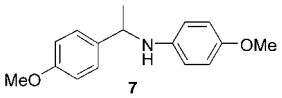
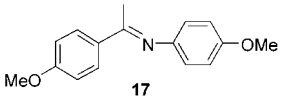
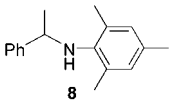
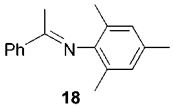
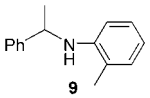
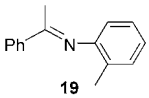
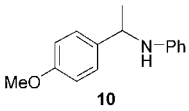
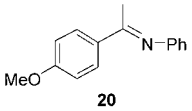
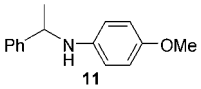
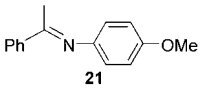
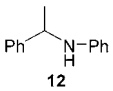
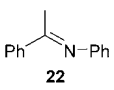
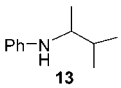
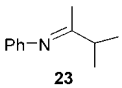
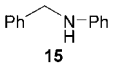
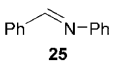
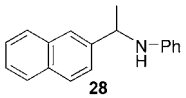
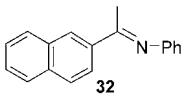
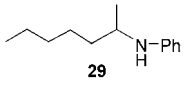
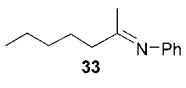
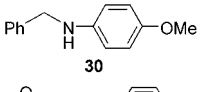
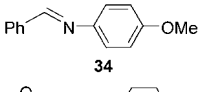
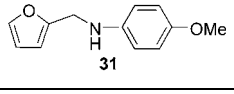
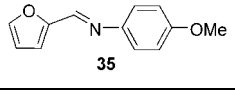
Entry	Substrate	Product	TOF[b] after 10 min [h^{-1}]	Yield [%] after 1 h[c]
1	 **7**	 **17**	71	>95
2	 **8**	 **18**	60	85
3	 **9**	 **19**	58	87
4	 **10**	 **20**	51	90
5	 **11**	 **21**	47	87
6	 **12**	 **22**	33	68
7	 **13**	 **23**	32[d]	44
8	 **14**	 **24**	31	38
9	 **15**	 **25**	24	30
10	 **16**	 **26**	<1	–
			60[e]	

[a] The reactions were carried out on a 0.125-mmol scale in toluene (1 mL) at 110 °C with 2 mol % of **3** and 1.5 equivalents of quinone **2a**. [b] TOF (turnover frequency) based on Ru. [c] Determined by ^{1}H NMR spectroscopy. [d] 4 mol % of **3** and 1.5 equivalents of quinone **2a** was used. [e] Run under microwave irradiation at 180 °C for 5 min.

high yields with catalytic amounts of **3**, **2a**, and **27** under air (Table 3).[33] Both ketimines (entries 1–7, 9, 10, Table 3) and aldimines (entries 8, 11, 12, Table 3) can be prepared from the corresponding amines. Amines with a secondary alkyl group reacted faster (to give ketimines) than those with a primary alkyl group (to give aldimines). Interestingly, also nonbenzylic amines can be used as substrates with high selectivity (entries 7 and 10, Table 3). Surprisingly, only traces of the hydrolyzed product were detected in the ^{1}H NMR spectrum for the unstable imine in entry 10 even after 12 h. A possible explanation why these rather unstable imines are not hydrolyzed in the present system, is that the water formed is continuously distilled off by the air stream used.

Table 3. Aerobic oxidation of amines using a biomimetic coupled catalytic system.[a]



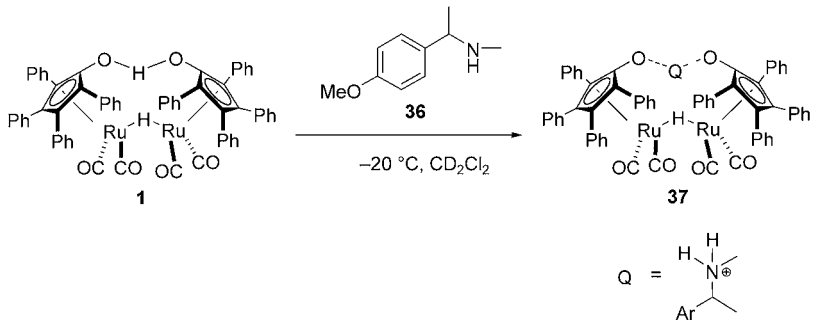
Entry	Substrate	Product	Time [h]	Yield [%][b]
1	 **7**	 **17**	6	90
2	 **8**	 **18**	6	86
3	 **9**	 **19**	12	95
4	 **10**	 **20**	6	88
5	 **11**	 **21**	6	88
6	 **12**	 **22**	12	90
7	 **13**	 **23**	12	83[c]
8	 **15**	 **25**	24	99[c,e]
9	 **28**	 **32**	12	84
10	 **29**	 **33**	12	76[c,d]
11	 **30**	 **34**	24	99[c,e]
12	 **31**	 **35**	24	99[e,f]

[a] Unless otherwise stated, the reactions were carried out on a 0.125-mmol scale in toluene (1 mL) at 110 °C with 2 mol % of **3**, 20 mol % of quinone **2a**, and 2 mol % of **27** under a steady flow of air. *Caution:* Air with toluene at 100 °C produces explosive mixtures in the gas phase. [b] Determined by ^{1}H NMR spectroscopy. [c] 4 mol % of **3** was used. [d] Traces of hydrolyzed product were observed in the ^{1}H NMR spectra. [e] The reactions were carried out on a 0.25-mmol scale in toluene (2 mL). [f] 8 mol % of **3** and 4 mol % of **27** were used.

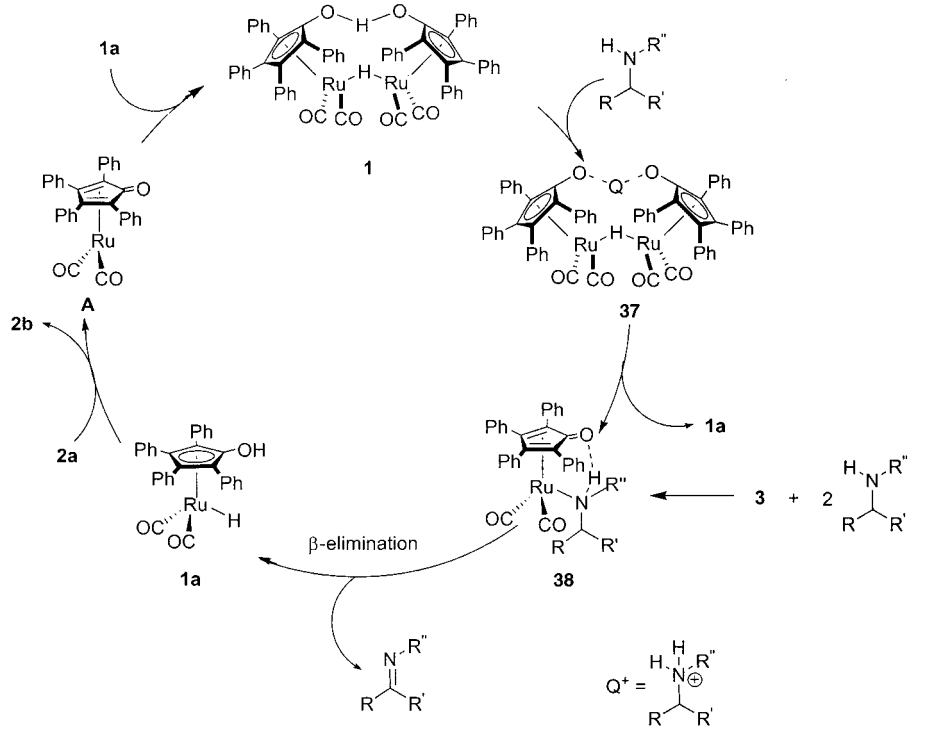
Mechanistic considerations: Complex **1** is one of the resting states with any of the catalysts in the first three entries in Table 1. To obtain catalysis with complex **1** it has to break up into **1a** and **A** under thermal conditions [Eq. (1)].[29,34] Interestingly, neither **1a** nor **A** have been observed under thermal conditions, which can be explained by a very low dissociation constant K_{diss} [Eq. (1)]. However attempts to dissociate catalyst **1** under thermal conditions failed without nucleophiles such as alcohols and amines, or hydrogen gas.

During a mechanistic study of **1a** with imines we found that **1** together with *N*-methyl-substituted amine **36** gave a new complex **37** at low temperatures (Scheme 5).[35] This is most likely the first step in the dissociation of dimer **1**.

With these results in hand, we propose an alternative catalytic cycle. Instead of thermal dissociation of **1**, the cycle starts with abstraction of a proton of **1** by an amine and replacement of the proton by the protonated amine to form complex **37** (Scheme 6).[36] This complex decomposes to form complexes **1a** and amine complex **38**. β-Elimination from the amine in **38** gives the corresponding imine and another molecule of **1a**. Quinone **2a** then oxidizes one of the two molecules of **1a** to **A**, which combines with **1a** to form the dimer **1** and this completes the catalytic cycle. When **3** is employed as the catalytic precur-



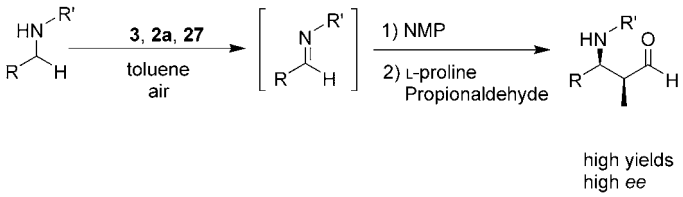
Scheme 5.



Scheme 6. Proposed mechanism for the ruthenium-catalyzed dehydrogenation of secondary amines ($Q^+ = [RR'CHNH_2R'']^+$.

sor the catalyst enters the catalytic cycle via complex **38**, which is formed from reaction of **3** with the amine.

Synthetic applications: As mentioned in the introduction, imines participate in a large number of synthetic transformations. The usual way of preparing imines is from the corresponding carbonyl compound and the appropriate amine, with removal of water under anhydrous conditions. The imine usually has to be isolated from this mixture before using it in the subsequent transformations. The biomimetic catalytic aerobic oxidation of amines reported here generates the imine from the amine without any stoichiometric reagents except molecular oxygen. These conditions are very favorable for using the imine in situ for further reactions. In a separate paper to be published elsewhere (Scheme 7),[37] we have demonstrated that the imines generated from the aerobic oxidation procedure can be conveniently used in an organocatalytic reaction without further purification. Removal of the solvent from the aerobic oxidation reaction and replacement with *N*-methylpyrrolidinone (NMP), followed by addition of L-proline and propionaldehyde gave *syn*-Mannich products in high yields and high *ee*.



Scheme 7.

Conclusion

We have developed an efficient catalytic process for the biomimetic aerobic oxidation of secondary amines that tolerates important substrate classes. Both aldimines and ketimines can be prepared by this methodology. Generally, electron-rich substrates react faster than electron-deficient substrates. The catalytic cycle for the transformation involves ruthenium–amine complexes as the key intermediates; it was shown that an amine can react with **1** to give complex **37**. The hydroquinone **2b** formed in Scheme 6 is continuously recycled to quinone **2a** in the aerobic process (cf. Scheme 3).

Experimental Section

^{1}H NMR spectra were recorded in $CDCl_3$ with a Varian XL-400 spectrometer using the residual peak of $CDCl_3$ ($\delta = 7.26$ ppm for ^{1}H) as internal standard. Ruthenium catalysts **1** and **3** were prepared according to reference [29]. Quinone **2a** was dried prior to use. Bis(salicylideniminato-3-propyl)methylaminocobalt(II) (**27**) was purchased from Aldrich and used as received. All other reagents are commercially available and were

used without further purification. Solvents were technical grade and distilled before use. The amines used were either commercially available or prepared by standard procedures. Spectral data for imines **17**,[38] **20, 22**, **23**, **24**, **25**, **32**, **33**,[31] and **34**, **35**[39] were in accordance with those previously reported.

Reference samples imines **18**, **19**, **21**, and **26** were prepared according to reference [31].

***N*-(2,4,6-trimethylphenyl)-(1-phenylethylidene)amine (18)**: ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C): δ = 8.02–8.05 (m, 2H), 7.45–7.50 (m, 3H), 6.89 (s, 2H), 2.30 (s, 3H), 2.08 (s, 3H), 2.00 ppm (s, 6H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C): δ = 165.6, 146.6, 139.5, 132.9, 130.3, 128.7, 128.5, 127.2, 125.7, 20.9, 18.1, 17.6 ppm.

***N*-(2-methylphenyl)-(1-phenylethylidene)amine (19)**: ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C): δ = 8.02–8.05 (m, 2H), 7.46–7.50 (m, 3H), 7.18–7.24 (m, 2H), 7.01–7.05 (m, 1H), 6.67–6.69 (m, 1H), 2.19 (s, 3H), 2.13 ppm (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C): δ = 165.1, 150.5, 139.6, 130.6, 130.5, 128.5, 127.3, 126.5, 123.4, 118.6 17.9, 17.6 ppm.

***N*-(4-methoxyphenyl)-(1-phenylethylidene)amine (21)**: ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C): δ = 7.95–7.97 (m, 2H), 7.43–7.45 (m, 3H), 6.90–6.92 (m, 2H), 6.74–6.77 (m, 2H), 3.82 (s, 3H), 2.25 ppm (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C): δ = 165.1, 156.1, 152.1, 140.0, 130.5, 128.5, 127.3, 120.9, 114.4, 55.7, 17.5 ppm.

***N*-(4-methoxyphenyl)-[1-(4-cyanophenyl)ethylidene]amine (26)**: ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C): δ = 8.05–8.08 (m, 2H), 7.72–7.75 (m, 2H), 6.91–6.94 (m, 2H), 6.74–6.77 (m, 2H), 3.83 (s, 3H), 2.28 ppm (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C): δ 164.1, 156.7, 144.1, 143.8, 132.4, 127.9, 120.9, 118.8, 114.5, 113.9, 55.7, 17.5 ppm.

General procedure for ruthenium-catalyzed dehydrogenation of amines with a stoichiometric amount of 2a: Ruthenium complex **3** (2.7 mg, 2.5 μmol, 2 mol %) and dry quinone **2a** (31.5 mg, 0.2 mmol, 1.5 equiv) were dissolved under an argon atmosphere in toluene (1 mL) in a round-bottomed flask equipped with a condenser and a stirring bar. Amine (0.125 mmol) was added and the reaction mixture was heated to 110 °C. The reaction course was monitored by ^{1}H NMR spectroscopy. The product was characterized by comparison with an authentic sample.

General procedure for the ruthenium-catalyzed aerobic oxidation of amines: Ruthenium complex **3** (4.2 mg, 2.5 μ mol, 2 mol %), quinone **2a** (4.2 mg, 25 μ mol, 20 mol %), and cobalt complex **27** (1 mg, 2.5 μmol, 2 mol %) were charged into a 5-mL round-bottomed flask under an argon atmosphere. The amine (1 mL, 0.125 M in toluene, 0.125 mmol) was added to this mixture followed by flushing with air for about 1 min. A stream of air was allowed to pass through the system, and the mixture was heated to 110 °C in an oil bath (reaction times are given in Table 3).[40] When the reaction was complete, the mixture was cooled to room temperature and analyzed by ^{1}H NMR spectroscopy. The product was characterized by comparison with an authentic sample.

[2,3,4,5-Ph$_4$(η^5-C$_4$CO)Ru(CO)$_2$N(CH$_3$)(CH(4-MeO-Ph)(CH$_3$))][2,3,4,5-Ph$_4$(η^5-C$_4$COH)Ru(CO)$_2$H] (37): Complex **1** (30 mg, 0.03 mmol) was weighed into an NMR tube, and CD_2Cl_2 (0.5 mL) was added under an argon atmosphere. The sample was cooled to −78 °C, **36** (0.03 mmol, 0.3 M, 0.1 mL) was added, then the sample was shaken carefully and inserted into the NMR spectrometer pre-cooled to −20 °C. Full conversion to **37** was observed. ^{1}H NMR (400 Hz, CD_2Cl_2, −20 °C): δ = −15.17 (s, 1H; RuH), 0.79 (s, 3H; NMe), 0.96 (br d, J = 6.4 Hz, 3H; CCH_3), 2.47 (br, 1H; CH), 3.78 (s, 3H; OCH_3), 6.80–7.26 (m, 44H; Ar), 8.91 (br s, 1H; NH), 9.56 ppm (br s, 1H; NH); ^{1}H NMR (400 Hz, CD_2Cl_2, 25 °C): δ = −16.27 (br s, 1H; RuH), 1.07 (br d, J = 7.3 Hz, 3H; CCH_3), 1.24 (s, 3H; NMe), 2.92 (br q, 1H; CH), 3.80 (s, 3H; OCH_3), 6.85–7.26 ppm (m, 44H; Ar).

Acknowledgements

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