ACS Catalysis

Letter

Cite This: ACS Catal. 2018, 8, 7734–7741

pubs.acs.org/acscatalysis

Synthesis of Pyrazines and Quinoxalines via Acceptorless Dehydrogenative Coupling Routes Catalyzed by Manganese Pincer Complexes

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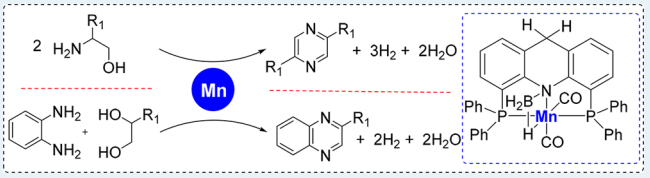
Supporting Information

ABSTRACT: Base-metal catalyzed dehydrogenative self-coupling of 2-amino alcohols to selectively form functionalized 2,5-substituted pyrazine derivatives is presented. Also, 2-substituted quinoxaline derivatives are synthesized by dehydrogenative coupling of 1,2-diaminobenzene and 1,2-diols. In both cases, water and hydrogen gas are formed as the sole byproducts. The reactions are catalyzed by acridine-based pincer complexes of earth-abundant manganese.



KEYWORDS: *manganese, pincer, pyrazine, quinoxaline, dehydrogenative coupling*

Aromatic *N*-heterocycles are found in diverse bioactive natural products and in essential intermediates for fragrances, pharmaceuticals, and agricultural chemicals.[1] Along with metal-free classical methods, metal-catalyzed multicomponent coupling or cyclization reactions were also developed for the production of *N*-heteroaromatic molecules.[2] Although synthetically useful, disadvantages of most of these reactions include multistep synthetic procedure, poor availability of starting materials, and copious waste generation. Alternative strategies based on one-step, sustainable, atom-economical efficient methodologies using inexpensive starting material for the preparation of valuable *N*-heteroaromatic molecules are desirable. In this regard, pyridine- or acridine-based pincer catalysts were explored by our group for several environmentally benign reactions with liberation of H_2 and/or water as the only by-products.[3] Indeed, notable progress has been made in recent years in sustainable synthesis of *N*-heteroaromatic molecules, such as substituted pyrrole, pyridine, benzimidazole, quinoline and pyrimidines derivatives, based on the acceptorless dehydrogenation of alcohols and amines using complexes based on noble metals, mainly Ir and Ru (see Scheme 1).[4−9]

The replacement of noble-metal-based catalysts by catalysts based on low-toxicity, earth-abundant base metals is a significant current direction in homogeneous catalysis. In recent years, base-metal catalysts were employed in various (de)hydrogenation reactions.[10] The synthesis of *N*-heteroaromatic compounds by dehydrogenative coupling of alcohols with amine derivatives catalyzed by base-metals were also reported.[11]

Pyrazines are an important class of *N*-heteroaromatic derivatives. Pyrazine derivatives show antibacterial, antitumor, and antibiotic activities, and they are also used in cancer experimental drugs.[12] Various types of polypyrazine derivatives are also used in the polymer industry as conjugated polymers.[13]

Methods for preparation of pyrazine derivatives are limited. Industrially, they are synthesized by condensation of ethylenediamine with vicinal diols such as propylene glycol using heterogeneous catalysts.[14a] The dehydrogenative coupling of α-amino carbonyl or α-diketones with vicinal diamines are the standard protocol for pyrazine synthesis.[15]

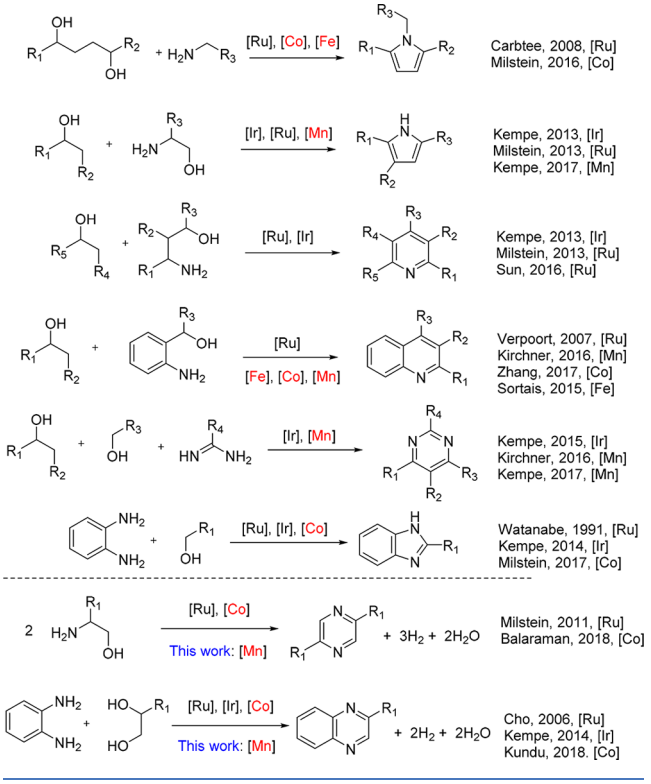
Pyrazines are also synthesized using α-halo ketones[16] or by the condensation reaction of diamines and epoxides.[17] Dehydrogenation of piperazines to form pyrazine derivatives was also reported using heterogeneous catalysts.[14a]

The dehydrogenative coupling of 2-amino-alcohols to form 2,5-disubstituted symmetrical pyrazines homogeneously catalyzed by a Ru(BPyPNN)-pincer complex was reported by our group.[18] Following the recent development of manganese-based catalysts in our laboratory,[19] we explored the possibility of dehydrogenative coupling of β-amino-alcohol derivatives. Recently, the synthesis of 2,5-diphenylpyrazine was reported via dehydrogenative coupling of 2-phenylglycinol catalyzed by a Co complex in the presence of a stoichiometric amount of base (with respect to substrate), generating stoichiometric waste, and requiring an extra post-reaction process for product isolation.[20] To the best of our knowledge, dehydrogenative self-coupling of β-amino alcohols to form 2,5-substituted pyrazine derivatives with the extrusion of H_2 and water catalyzed by a complex of an earth-abundant metal and a catalytic amount of base has not been reported. Herein, we

Received: June 6, 2018
Revised: July 19, 2018
Published: July 23, 2018

DOI: 10.1021/acscatal.8b02208
ACS Catal. 2018, 8, 7734−7741

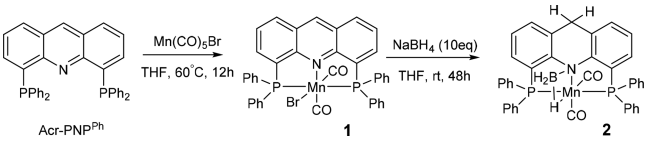
Scheme 1. Synthesis of *N*-Heteroaromatics via Dehydrogenative Coupling of Alcohols and Amines Catalyzed by Noble- or Base-Metal Complexes



present an acridine-based manganese pincer complex that catalyzes the formation of pyrazines by dehydrogenative coupling of 1,2-aminoalcohol derivatives, as well as the formation of quinoxalines by dehydrogenative coupling of 1,2-diaminobenzene with 1,2-vicinal diols.

Treatment of our previously reported Acr-PNP^{Ph} (Acr-PNP^{Ph} = 4,5-bis(diphenylphosphino)-acridine, HAcr-PNP^{Ph} = 4,5-bis(diphenylphosphino)-9H-acridine-10-ide) ligand[21] with $Mn(CO)_5Br$ at 60 °C in THF led to the formation of a new manganese complex $Mn(Acr\text{-}PNP^{Ph})(CO)_2Br$ (**1**) in 96% yield (Scheme 2). Single crystals of **1** suitable for X-ray

Scheme 2. Synthesis of Complex 1 and 2



diffraction (XRD) were obtained by slow evaporation of a saturated solution of THF. The X-ray structure of **1** exhibits an octahedral geometry with meridional coordination of the Acr-PNP^{Ph} ligand, two mutually cis carbonyl ligands and a bromide ligand (see Figure 1, as well as the Supporting Information (SI)).

Interestingly, the reaction of complex **1** with an excess of sodium borohydride formed the novel azaborametallacyclic complex **2**. Only a few complexes bearing such an azaborametallacycle are known.[22] The reduction of the acridine ring in the C9 position was clearly confirmed by the ^{1}H NMR spectrum. In addition, a sharp peak at −7.4 ppm (corresponding to one proton) and a broad peak at 2.1 ppm

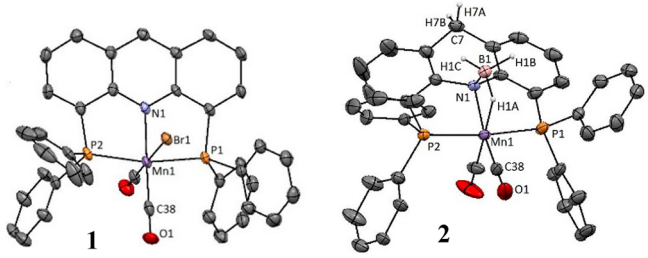


Figure 1. X-ray structure of complexes **1** and **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected hydrogen atoms are omitted for clarity. For selected bond lengths and angles, see the SI.

(corresponding to two protons) indicate the presence of the BH_3 moiety. The presence of the two mutually cis carbonyl ligands was confirmed by IR spectroscopy (1940 cm^{-1}, 1868 cm^{-1}, 1:1 for *cis* CO, and 2424 cm^{-1}, 2347 cm^{-1} for BH_3 moiety). Single crystals of **2** suitable for XRD study were obtained by slow diffusion of pentane into a saturated solution of **2** in THF at −30 °C. The molecular structure exhibits an octahedral geometry with meridional coordination of the dearomatized HAcr-PNP^{Ph} ligand. The two carbonyl ligands occupy cis positions of the octahedral metal center. The BH_2 group forms a bridging unit between the acridine-N atom and one of the manganese-bound hydrides (H1a) forming a four-membered metallacycle. The Mn−Ha bond distance is 1.708 Å and the Mn···B distance is 2.309 Å. The nitrogen atom of the ligand is coordinated to the metal center and to the boron atom of the BH_3 moiety (B−N = 1.578 Å, Mn−N = 2.077 Å). One of the hydride ligands (H) that bridges between manganese and boron shows a considerably longer B−H bond (1.238 Å) than the other two B−H bonds (1.067 and 1.124 Å) in the BH_3 moiety.

To explore the catalytic activity, a toluene solution of 2-phenylglycinol was heated at 150 °C for 24 h in the presence of complex **2** (2 mol %) and KH as base (3 mol %) in a closed system, affording 2,5-diphenylpyrazine in 99% yield, as determined by GCMS (Table 1, entry 1). Using THF or 1,4-dioxane as a solvent under the same condition resulted in 90% and 95% yields of the product, respectively (Table 1, entries 2 and 3). Lowering the reaction temperature to 125 °C for 24 h resulted in quantitative product formation in toluene. Similarly, when the reaction time was reduced to 12 h under the same conditions at 150 °C in toluene, a quantitative formation of product was observed (Table 1, entries 4 and 5). A reaction conducted in an open system under Ar flow resulted in 92% conversion, indicating that the evolved hydrogen in a closed system does not affect the reaction process significantly (Table 1, entry 6). In the absence of any base, under the same conditions, only a trace amount of 2,5-diphenylpyrazine was detected (Table 1, entry 7). Using ^{t}BuOK and NaOMe under the optimized conditions resulted in poor yields (15% and 10%, respectively), whereas using NaOEt resulted in 81% yield of the product 2,5-diphenylpyrazine under the same conditions (Table 1, entries 8−10). Significantly, the addition of 300 equiv of Hg to the catalytic solution showed no decrease in product formation or selectivity (Table 1, entry 11), which was suggestive of a homogeneous catalytic pathway.

Our previously reported PNP, PNNH, and PNHP−Mn pincer complexes **3**,[19a] **4**,[19d] and **5**[19c] (Table 1) were then screened. Surprisingly, using the ^{t}Bu-substituted complex **3** resulted in only 24% yield of 2,5-diphenylpyrazine at 150 °C

DOI: 10.1021/acscatal.8b02208
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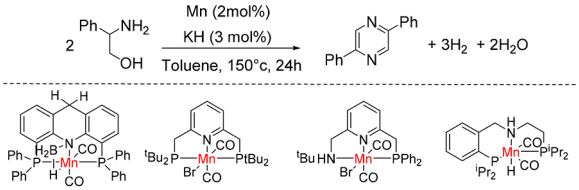
Table 1. Optimization of the Reaction Conditions for Pyrazine Synthesis[a]



2 3 4 5

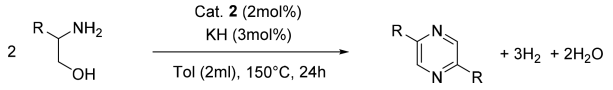
entry	catalyst (2 mol %)	base (3 mol %)	yield[b] (%)
1	**2**	KH	99
2[c]	**2**	KH	90
3[d]	**2**	KH	95
4[e]	**2**	KH	99
5[f]	**2**	KH	99
6[g]	**2**	KH	92
7	**2**		05
8	**2**	^{t}BuOK	15
9	**2**	NaOMe	10
10	**2**	NaOEt	81
11[h]	**2**	KH	99
12	**3**	KH	24
13	**4**	KH	23[i]
14	**5**	KH	64
15	**1**	KH	95

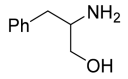
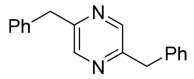
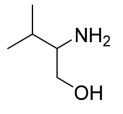
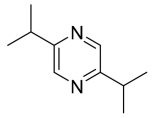
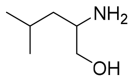
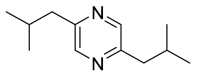
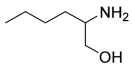
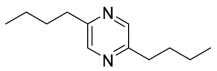
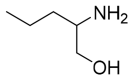
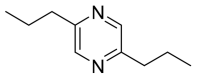
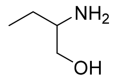
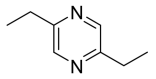
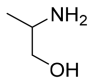
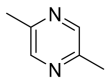
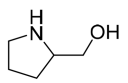
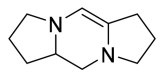
[a]Reaction conditions: catalyst (2 mol %), 2-phenylglycinol (0.5 mmol), base (3 mol %), 150 °C, 24 h, toluene (2 mL). [b]GC-MS yield with mesitylene as an internal standard. [c]Solvent THF. [d]Solvent 1,4-dioxane. [e]Reaction temperature 125 °C, for 24 h. [f]Reaction time = 12 h. [g]Open system under Ar flow at 125 °C (bath temperature). [h]In the presence of 300 equiv of Hg. [i]Unidentified products were formed; total conversion = 40%.

(Table 1, entry 12), probably because of steric hindrance, whereas the PNNH-Mn catalyst **4** produced 23% of the pyrazine derivative at 40% conversion, with the formation of some unidentified products (Table 1, entry 13). Complex **5** selectively yielded 64% of the 2,5-diphenylpyrazine as product (Table 1, entry 14). Complex **1** was also used as catalyst under same conditions, yielding 95% of the product (Table 1, entry 15).

Using the optimized reaction conditions, in the presence of catalyst **2** (2 mol %) and 3 mol % of KH in toluene at 150 °C (bath temperature), various *β*-amino alcohols were studied in a closed system. Employing 2-amino-3-phenylpropane1-ol resulted in 95% yield of the 2,5-dibenzylpyrazine product (Table 2, entry 1), whereas upon use of 2-amino-3-methylbutane-1-ol 86% yield of the 2,5-diisopropylpyrazine product was obtained (Table 2, entry 2). Reaction of 2-amino-4-methylpentane-1-ol yielded 80% of the corresponding pyrazine derivative under the optimized reaction conditions (Table 2, entry 3). 2-Amino-1-hexanol and 2-amino-1-pentanol as substrates yielded 65% and 95% of the corresponding pyrazine derivatives, respectively (Table 2, entries 4 and 5). 2-Aminobutane-1-ol gave 40% of the 2,5-diethylpyrazine product, whereas use of 2-amino-propane-1-ol resulted in full conversion, yielding 45% of the 2,5-dimethylpyrazine product (Table 2, entries 6 and 7). The difference in *β*-amino alcohol conversion and yield of product pyrazine, as observed in Table 2, indicates the formation of a mixture of unidentified products. Using pyrrolidin-2-yl-methanol as a substrate afforded the tricyclic ring system. 2,3,5a,6,7,8-Hexahydro-1H,5H-dipyrrolo[1,2-a:1′,2′-d]-

Table 2. Pyrazines Synthesis from *β*-Amino Alcohols Catalyzed by Complex 2[a]



Entry	Substrate	Product	Conv. (%)	Yield[b] (%)
1			99	95
2			99	86
3			99	80
4			99	65
5			99	95
6[c]			99	40
7[c]			99	45
8[c]			65	30

[a]Optimized reaction conditions: Catalyst **2** (2 mol %), *β*-amino alcohol (0.5 mmol), KH (3 mol %), 150 °C, 24h, toluene. [b]Isolated yield. [c]Reaction time = 48 h, detected by GC-MS.

pyrazine was detected in 30% yield with other unidentified side products (Table 2, entry 8). At this point, we should mention that the sulfur functionalized methioninol was not reactive under the same reaction conditions. No trace of the corresponding pyrazine derivatives was found, only 10% of defunctionalized 2,5-diethylpyrazine was observed, with the rest being unreacted methioninol.

Benzopyrazine, also named quinoxaline, is a heterocyclic compound containing a fused benzene ring with a pyrazine ring. The development of efficient methods for the synthesis of quinoxalines is essential due to their significant application in several fields, including pharmaceuticals and advanced materials. The well-established method for quinoxalines synthesis is the condensation of 1,2-aryldiamines with 1,2-dicarbonyl compounds to afford good to moderate yields.[23] Many improved methods have been reported using various approaches.[24] The dehydrogenative approach for quinoxalines from 1,2-phenylenediamines and vicinal-diols was studied using noble-metal catalysts; however, in all cases, more than a stoichiometric amount of base was needed.[8b,9] Recently, a similar transformation catalyzed by a Co complex was reported, requiring a stoichiometric amount of base and excess of diol, which generates waste and exhibits poor atom economy.[25] Here, we explore the dehydrogenative coupling

DOI: 10.1021/acscatal.8b02208
ACS Catal. 2018, 8, 7734−7741

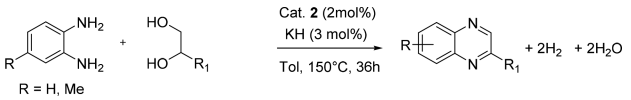
reaction of 1,2-diaminobenzene and vicinal 1,2-diol derivative by catalyst **2** under the above-mentioned optimized conditions.

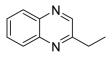
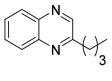
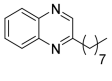
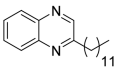
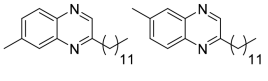
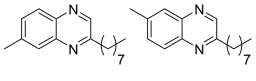
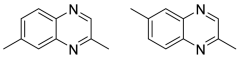
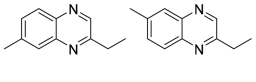
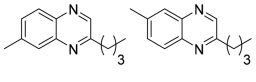
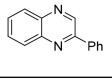
The treatment of an equivalent amount of 1,2-diaminobenzene and 1,2-butanediol in the presence of catalyst **2** (2 mol %) and KH (3 mol %) at 150 °C for 36 h in a closed system afforded 2-ethylquinoxaline (95%) as the product (Table 3, entry 1). Under the same conditions 1,2-hexanediol afforded 2-butylquinoxaline (40%) with 5% hydrogenated product 2-butyl-1,2,3,4-tetrahydroquinoxaline (Table 3, entry 2). 1,2-Decanediol afforded 94% (Table 3, entry 3) conversion, where 49% of the corresponding quinoxaline derivative and 24% of the hydrogenated product were formed, in addition to unidentified high-molecular-weight products. 1,2-Tetradecanediol underwent 95% conversion to form the quinoxaline product (65%) and the hydrogenated product (35%) (Table 3, entry 4). 4-Methyl-1,2-diaminobenzene exhibited similar activity with the long-chain vicinal diol substrate to form the corresponding quinoxaline derivative. With 1,2-tetradecanediol and 1,2-decanediol as substrates, 75% and 74% of the corresponding quinoxaline derivatives were formed as major products, respectively, together with their two hydrogenated isomers (Table 3, entries 5 and 6; for isomer details, see the SI).

Although long-chain vicinal diols are effective using a catalytic amount of base, the short-chain 1,2-diols require stoichiometric amounts of base to form the corresponding quinoxaline product. Reaction of 1,2-propanediol (0.5 mmol) and 1,2-diaminobenzene (0.5 mmol) in the presence of 0.5 mmol of KH and catalyst **2** afforded 90% 2-methylquinoxaline (Table 3, entry 7). Ethylene glycol afforded 35% of the quinoxaline as the final product (Table 3, entry 8). The substituted 4-methyl-1,2-diaminobenzene also shows the same activity with 1,2-propanediol and 1,2-butanediol as substrates, affording 78% and 82% of the corresponding quinoxaline derivatives, respectively (Table 3, entries 9 and 10). Reaction of 1,2-hexanediol with 4-methyl-1,2-diaminobenzene resulted in 99% conversion, including 80% of the corresponding quinoxaline product and 20% of the hydrogenated 2-butyl-6-methyl-1,2,3,4-tetrahydroquinoxaline product (Table 3, entry 11). The treatment of 1,2-diaminobenzene and 1-phenyl-1,2-ethanediol afforded 2-phenylquinoxaline (75%) as the product under similar conditions (Table 3, entry 12).

To gain mechanistic insight of the pyrazine and quinoxaline formation reactions by the dehydrogenative coupling, some control experiments were performed. Treatment of benzyl alcohol in the presence of catalyst **2** (2 mol %) and a catalytic amount of base (KH, 3 mol %) at 150 °C for 24 h in a closed system afforded benzyl benzoate as the final product (99%) (see Scheme 3a). The reaction of 0.5 mmol of benzyl alcohol and 0.5 mmol of 1-hexylamine in the presence of catalyst **2** (2 mol %) and KH (3 mol %) at 150 °C for 24 h in a closed system afforded a quantitative amount of *N*-benzylidenehexylamine as the only product (see Scheme 3b). These

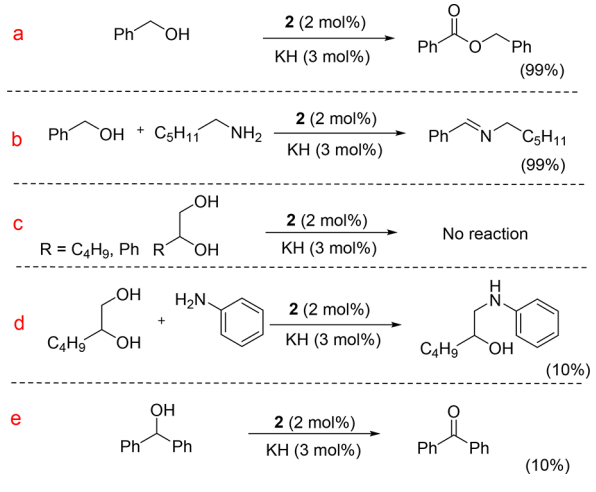
Table 3. Synthesis of Quinoxalines from 1,2-Diaminobenzene and 1,2-Diols[a]



Entry	Alcohols	Products	Conv. (%)	Yield (%)[b]
1			99	95
2			45	40 (5)
3			94	49 (24)
4			95	65 (35)
5[c]			99	75
6[c]			94	74 (17)
7[d]			85	80
8[d]			70	35
9[c,d]			80	78
10[c,d]			85	82
11[c,d]			99	80 (20)
12[d]			85	75 (8)

[a]Optimized reaction conditions: catalyst **2** (2 mol %), KH (3 mol %), 1,2-diaminobenzenes (0.5 mmol), 1,2-diols (0.5 mmol), 150 °C (bath temperature), 36 h, toluene. [b]Isolated yield (hydrogenated product shown in parentheses). [c]4-Methyl-1,2-diaminobenzene as a substrate. [d]Base (KH) used = 0.5 mmol.

Scheme 3. Control Experiments



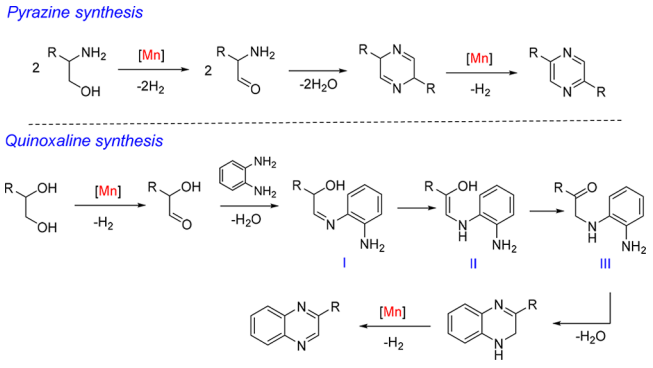
DOI: 10.1021/acscatal.8b02208
ACS Catal. 2018, 8, 7734−7741

experiments show that catalyst **2** can efficiently catalyze the dehydrogenative coupling of the alcohol.

In a control experiment, using only 1,2-hexanediol or 1-phenyl-1,2-ethanediol and catalyst **2** and base, no reaction occurred under the optimized reaction conditions (see Scheme 3c). However, treatment of an equivalent amount of 1,2-hexanediol and aniline in the presence of catalyst **2** under the same conditions afforded 10% of 1-(phenylamino)hexan-2-ol (Scheme 3d), indicating that the dehydrogenation equilibrium of the vicinal diol is unfavorable and is shifted by coupling with the amine reactant. In another control experiment, under the same conditions, diphenylmethanol afforded only 10% of benzophenone as the dehydrogenated product, which indicates that dehydrogenation of the primary alcohol is more favorable than that of the secondary alcohol (see Schemes 3e and 3a).

According to our observations, a plausible mechanism of the organic intermediates involved is proposed in Scheme 4.

Scheme 4. Proposed Mechanism for the Dehydrogenative Coupling Reactions Leading to the Formation of Pyrazine and Quinoxaline

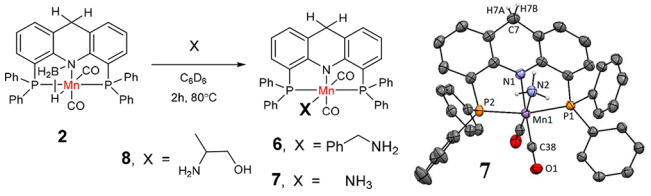


Dehydrogenation of the *β*-amino alcohol derivative catalyzed by **2** yields an aldehyde intermediate that undergoes self-coupling with another molecule, leading to 2,5-dihydropyrazine derivatives via the elimination of two molecules of water. The 2,5-dihydropyrazine then undergoes rapid metal-catalyzed dehydrogenation, eliminating a molecule of dihydrogen and forming a stable aromatic pyrazine derivative. Formation of the cyclic intermediate was confirmed when pyrrolidin-2-yl-methanol was employed in the reaction, leading to 2,3,5a,6,7,8-hexahydro-1H,5H-dipyrrolo[1,2-a:1′,2′-d]pyrazine (molecular mass = 164) as a product, since the further dehydrogenation to form the aromatic pyrazine is not possible for this substrate (see Table 2, entry 8).

The dehydrogenative coupling of 1,2-diaminobenzene and vicinal diols to form quinoxalines also follows initial dehydrogenation of the terminal alcohol group of the 1,2-diol system. Condensation of the amine group of the 1,2-diaminobenzene with the carbonyl moiety leads to intermediate **I** that, upon a proton shift, forms **II**, which undergoes tautomerization to intermediate **III** (see Scheme 4). Condensation with a second amine group leads to the formation of a 1,2-dihydroquinoxaline derivative, which undergoes rapid dehydrogenation to form the quinoxaline derivative as the final product.

In order to gain further mechanistic insight, we tried to isolate possible active organometallic amido intermediate without the boron-bridged moiety. The treatment of catalyst **2** with 2 equiv of benzyl amine for 2 h at 80 °C showed a new peak in ^{31}P NMR spectroscopy at 78.6 ppm. Interestingly, ^{1}H NMR spectroscopy showed the disappearance of the bound B*H* signal of complex **2** at −7.4 ppm, which is suggestive of the displacement of the bound BH moiety by benzyl amine and formation of complex **6**. However, attempts to isolate the new complex **6** were not successful. The bridged BH_3 moiety was completely intact when complex **2** was treated with excess of NEt_3 or any primary alcohol. On the other hand, upon treatment of **2** with NH_3 (1 bar), the bridged BH_3 peak at −7.4 ppm in the ^{1}H NMR spectrum disappear upon heating the reaction mixture at 80 °C for 30 min, whereas little shift was observed in the ^{31}P NMR spectrum. The ^{11}B NMR spectrum showed a doublet at 28.1 ppm and a singlet at 25.4 ppm, which could possibly result from the dehydrogenated product of the ammonia−borane adduct. Finally, crystallization from pentane THF mixture at −30 °C afforded yellow crystals of complex **7** in 85% yield (see Scheme 5). XRD analysis unambiguously

Scheme 5. Synthesis of Complexes 6, 7, and 8



showed a neutral octahedral ammonia-coordinated manganese complex **7** bearing a hydrogenated acridine ring containing a pincer ligand and two mutually cis CO ligands. Single-crystal X-ray structure revealed a long-range hydrogen bonding (2.546 Å) between a proton of ammonia and the acridine nitrogen, which suggests that the weakly basic acridine nitrogen may be capable of accepting the hydroxy proton of the alcohol during the alcohol dehydrogenation process (see the SI for the mechanism). Complexes **6** and **7** do not dehydrogenate the alcohol under neutral conditions, whereas both the complexes are equally active compared to **2** for the pyrazine formation reaction in the presence of catalytic amount of base. A toluene solution of 2-phenylglycinol was heated at 150 °C for 24 h in the presence of the isolated complex **7** (2 mol %) without any base in a closed system afforded only 8% of the 2,5-diphenylpyrazine (the amino group of 2-phenylglycinol acts as a weak base; see the next experiment), whereas the addition of 3 mol % KH as the base afforded 99% of the product under the same conditions. Under the similar condition *in situ* generated complex **6** and base also showed the similar activity with 99% yield of the 2,5-diphenylpyrazine. Treatment of complex **2** with 2 equiv of 2-amino-1-propanol in a sealed NMR tube afforded a new complex **8**, which is probably the amine-bound species showing a peak at 76.4 ppm in ^{31}P NMR spectroscopy, along with a broad peak at 72 ppm. The addition of a base to the reaction mixture and heating afforded the pyrazine derivative as detected by GCMS. To obtain the active amido intermediate, complex **1** was treated with NaH in the presence of benzyl alcohol in THF.[26] However, a tricarbonyl Mn complex bearing a reduced acridine ligand, which is not catalytically active, was obtained (see the SI for details). Alternatively, treatment of **1** with an equivalent of $NaBEt_3H$ afforded an unstable Mn−H compound (−5.2 ppm in ^{1}H NMR, and 90.2 ppm in ^{31}P NMR spectroscopy) that undergoes rapid reductive disproportionation to form an NMR silent compound. Reaction of complex **2** in the presence

DOI: 10.1021/acscatal.8b02208
ACS Catal. 2018, 8, 7734−7741

of alcohol and a catalytic amount of base afforded a broad signal at 72 ppm in the ^{31}P NMR spectrum but complete characterization of the generated species was unsuccessful. A five-coordinated amido species may play an active role in the alcohol dehydrogenation process, and, because of the less basic nature of the amido nitrogen of the ligand, alkoxide-assisted alcohol dehydrogenation and dihydrogen liberation mechanism probably occur (see the SI).

In conclusion, 2,5-dialkyl-substituted symmetrical pyrazine derivatives were synthesized by the dehydrogenative self-coupling of 2-aminoalcohols. Quinoxaline derivatives were also synthesized by dehydrogenative coupling of 1,2-diaminobenzene and 1,2-diols. Both reactions are catalyzed by a novel complex of the earth-abundant manganese, complex **2**, and generate hydrogen gas and water as the only byproducts, making these synthetic methods atom-economical, environmentally benign, and sustainable. The relevant acridine-based manganese complexes were also prepared. The reaction plausibly proceeds via alcohol dehydrogenation, followed by coupling with amines.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b02208.

Experimental procedure, GC-MS, NMR spectra of organic products (PDF)

Crystal data of complexes **1**, **2**, and **7** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the European Research Council (ERC AdG 692775). D.M. holds the Israel Matz Professorial Chair. P.D. and A.K. are thankful to the Planning and Budgeting Committee (PBC) for a postdoctoral fellowship. N. A. E.-J. thanks Mr. Armando Jinich for a postdoctoral fellowship.

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DOI: 10.1021/acscatal.8b02208
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