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Letter

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ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.8b02208 • Publication Date (Web): 23 Jul 2018

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

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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 by-products. The reactions are catalyzed by acridine-based pincer complexes of earth-abundant manganese.

KEYWORDS. Manganese, Pincer, Pyrazine, Quinoxaline, Dehydrogenative Coupling

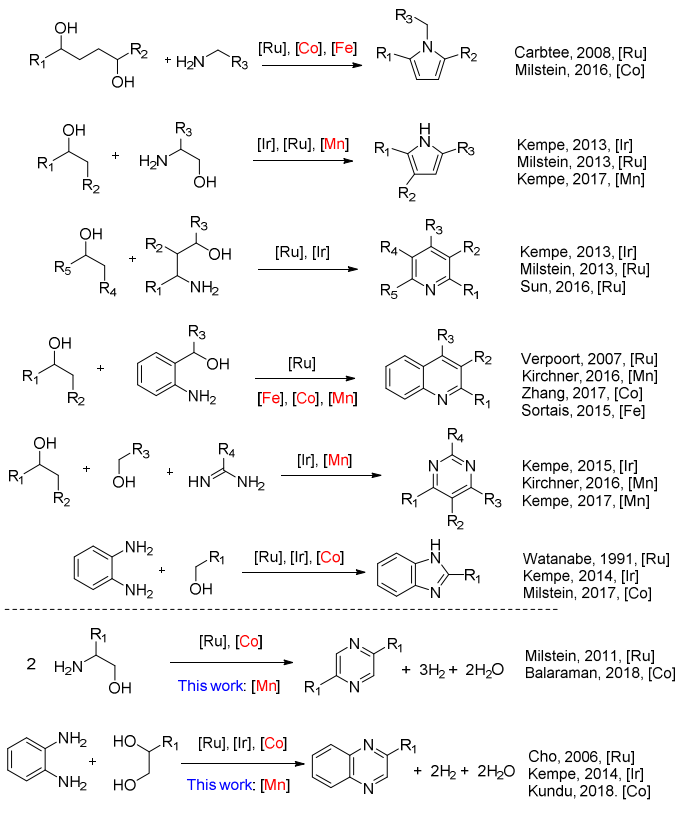
Aromatic N-heterocycles are found in diverse bioactive natural products and in essential intermediates for fragrances, pharmaceuticals, and agricultural chemicals.[1] Along with metal free classical methods, metal-catalyzed multicomponent coupling or cyclization reactions were also developed for the production of N-heteroaromatic molecules.[2] Although synthetically useful, disadvantages of most of these reactions include multi-step 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 (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 are also used in cancer experimental drugs.[12] Various types of poly-pyrazine 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]

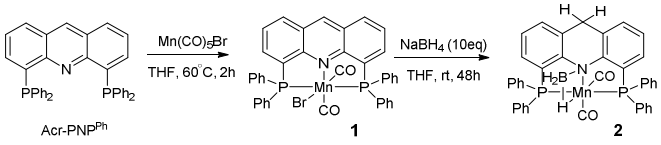
Pyrazines are also synthesized using α-halo ketones[16] or by the condensation reaction of diamines and epoxides[17]. Dehydrogenation of piperazines to form pyrazine derivatives was also reported using heterogeneous catalysts.[14a]



Scheme 1. Synthesis of N-Heteroaromatics via dehydrogenative coupling of alcohols and amines catalyzed by noble- or base- metal complexes

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 lab[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 present an acridine-based manganese pincer complex which catalyzes formation of pyrazines by dehydrogenative coupling of 1,2-aminoalcohol derivatives, as well as 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-PNP^{Ph})$(CO)_2$Br (**1**) in 96% yield (Scheme 2). Single crystals of **1** suitable for X-ray diffraction 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 (Figure 1; see also the Supporting Information (SI)).



Scheme 2. Synthesis of complex 1 and 2

Interestingly, reaction of complex **1** with 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 (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 (1940cm^{-1}, 1868cm^{-1}, 1:1 for *cis* CO, and 2424cm^{-1}, 2347cm^{-1} for BH_3 moiety). Single crystals of **2** suitable for X-ray diffraction 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 (Ha) 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 = 1.578Å, Mn−N = 2.077Å). One of the hydride ligands (H) which bridges between manganese and boron shows a considerably longer B-H bond (1.238Å) than the other two B-H bonds (1.067 Å and 1.124 Å) in the BH_3 moiety.

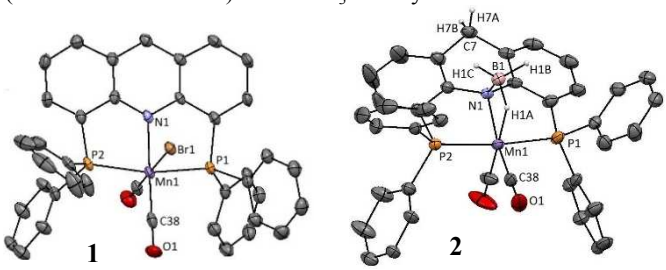


Figure 1. X-ray structure of complexes **1** and **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected hydrogen atoms are omitted for clarity. For selected bond lengths and angles, see the SI.

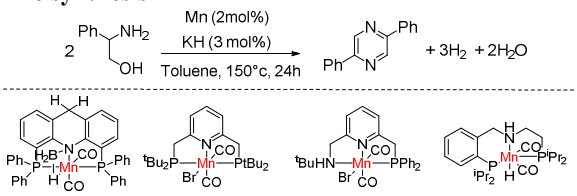
To explore the catalytic activity, a toluene solution of 2-phenylglycinol was heated at 150°C for 24h in the presence of complex **2** (2 mol%) and KH as base (3 mol%) in a closed system, affording 2,5-diphenylpyrazine in 99% yield as determined by GCMS (Table 1, entry 1). Using THF or 1,4-dioxane as solvents under the same condition resulted in 90% and 95% yields of the product, respectively (entries 2, 3). Lowering the reaction temperature to 125°C for 24h resulted in quantitative product formation in toluene. Similarly, when the reaction time was reduced to 12h under the same conditions at 150°C in toluene quantitative formation of product was observed (entry 4, 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 (entry 6). In absence of any base under the same conditions only a trace amount of 2,5-diphenylpyrazine was detected (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 same conditions (entry 8-10). Significantly, addition of 300 equivalents of Hg to the catalytic solution showed no decrease in product formation or selectivity (Table 1, entry 11), 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 (Table 1, entry 12), probably due to steric hindrance, whereas the PNNH-Mn catalyst **4** produced 23% of the pyrazine derivative at 40% conversion, with formation of some unidentified products (entry 13). Complex **5** yielded selectively 64% of the 2,5-diphenylpyrazine as product (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 pyra-

zine derivative under the optimized reaction conditions (Table 2, entry 3).

Table 1. Optimization of the reaction conditions for pyrazine synthesis[a]



2 3 4 5

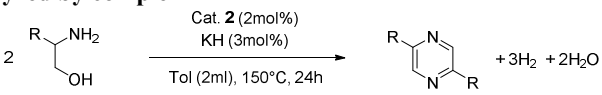
Entry	Catalyst (2 mol%)	Base (3 mol%)	Yield[b] (%)
1	**2**	KH	99
2[c]	**2**	KH	90
3[d]	**2**	KH	95
4[e]	**2**	KH	99
5[f]	**2**	KH	99
6[g]	**2**	KH	92
7	**2**	-	05
8	**2**	^{t}BuOK	15
9	**2**	NaOMe	10
10	**2**	NaOEt	81
11[h]	**2**	KH	99
12	**3**	KH	24
13	**4**	KH	23[i]
14	**5**	KH	64
15	**1**	KH	95

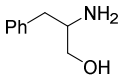
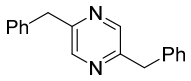
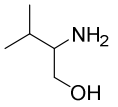
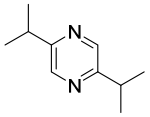
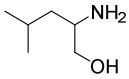
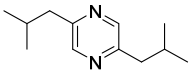
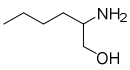
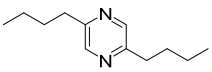
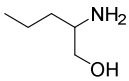
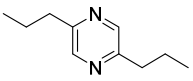
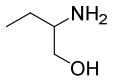
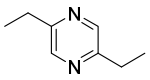
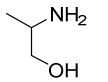
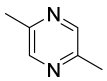
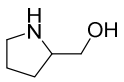
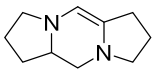
[a]Reaction conditions: Catalyst (2 mol%), 2-phenylglycinol (0.5mmol), base (3 mol%), 150°C, 24h, toluene (2ml), [b]GC-MS yield with mesitylene as internal standard, [c]solvent THF, [d]solvent 1,4-dioxane, [e]reaction temperature 125°C, for 24h, [f]reaction time 12h, [g]open system under Ar flow at 125°C (bath temp.), [h]in presence of 300 equiv. of Hg, [i]unidentified products formed, total conversion 40%.

2-Amino-1-hexanol and 2-amino-1-pentanol as substrates yielded 65% and 95% of the corresponding pyrazine derivatives, respectively (entries 4, 5). 2-aminobutane-1-ol gave 40% of the 2,5-diethylpyrazine product whereas use of 2-aminopropane-1-ol resulted in full conversion yielding 45% of the 2,5-dimethylpyrazine product (Table 2, entry 6, 7). The difference in β-amino alcohol conversion and yield of product pyrazine as observed in Table 2 indicates formation of a mixture of unidentified products. Using Pyrrolidin-2-yl-methanol as substrate afforded the tricyclic ring system. 2,3,5a,6,7,8-hexahydro-1H,5H-dipyrrolo[1,2-a:1',2'-d]pyrazine in 30% yield with other unidentified side products (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, 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 but 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 generate waste and exhibits poor atom economy.[25] Here we explore the dehydrogenative coupling reaction of 1,2-diaminobenzene and vicinal 1,2-diol derivative by catalyst **2** under the above mentioned optimized condition.

Table 2. Pyrazines synthesis from β-amino alcohols catalyzed by complex 2[a]



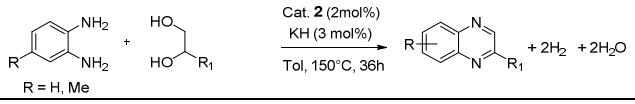
Entry	Substrate	Product	Con (%)	Yield[b] (%)
1			99	95
2			99	86
3			99	80
4			99	65
5			99	95
6[c]			99	40
7[c]			99	45
8[c]			65	30

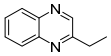
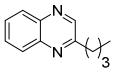
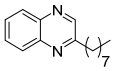
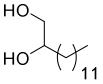
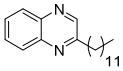
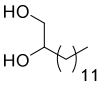
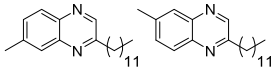
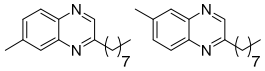
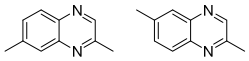
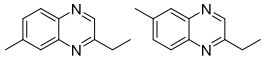
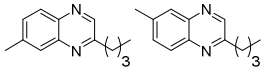
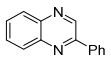
[a]Optimized reaction conditions: Catalyst **2** (2 mol%), β-amino alcohol (0.5 mmol), KH (3 mol%), 150°C, 24h, toluene, [b]Isolated yield. [c]reaction time 48h detected by GC-MS.

The treatment of an equivalent amount of 1,2-diaminobenzene and 1,2-butanediol in presence of catalyst **2** (2 mol%) and KH (3 mol%) at 150°C for 36h in a closed system afforded 95% of 2-ethylquinoxaline as the product (Table 3, entry 1). Under the same conditions 1,2-hexanediol afforded 40% of 2-butylquinoxaline with 5% of the hydrogenated product 2-butyl-1,2,3,4-tetrahydroquinoxaline (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 65% of the quinoxaline product and 35% the hydrogenated product (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 (entries 5, 6, for isomer details see SI).

Table 3. Synthesis of quinoxalines from 1,2-diaminobenzene and 1,2 diols[a]



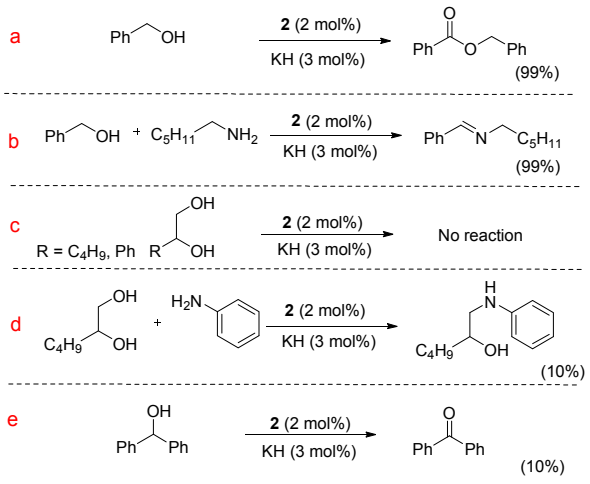
Entry	Alcohols	Products	Con (%)	Yield (%)[b]
1			99	95
2			45	40 (5)
3			94	49 (24)
4			95	65 (35)
5[c]			99	75
6[c]			94	74 (17)
7[d]			85	80
8[d]			70	35
9[c,d]			80	78
10[c,d]			85	82
11[c,d]			99	80 (20)
12[d]			85	75 (8)

[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), 36h, toluene, [b]Isolated yield (In parenthesis hydrogenated product). [c]4-methyl-1,2-diaminobenzene as substrate. [d]Base (KH) used 0.5 mmol,

Although long chain vicinal diols are effective using a catalytic amount of base, the short chain 1,2 diols require stoichiometric amount of base to form the corresponding quinoxaline product. Reaction of 1,2-propanediol (0.5mmol) and 1,2-diaminobenzene (0.5 mmol) in presence of 0.5 mmol of KH and catalyst **2** afforded 90% of 2-methylquinoxaline (Table 3, entry 7). Ethylene glycol afforded 35% of the quinoxaline as the final product (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 (entries 9, 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 (entry 11). The treatment of 1,2-diaminobenzene and 1-phenyl-1,2-ethanediol afforded 75% of the 2-phenylquinoxaline as the product under similar condition (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 24h in a closed system afforded benzyl benzoate as the final product (99%) (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 (Scheme 3b). These 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 took place under the optimized reaction conditions (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 (Scheme 3e and 3a).

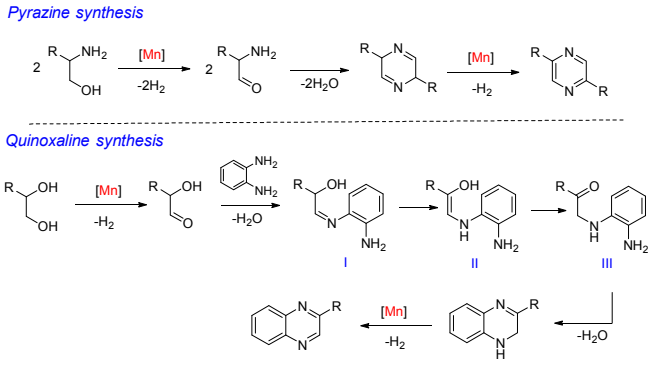


Scheme 3. Control experiments

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

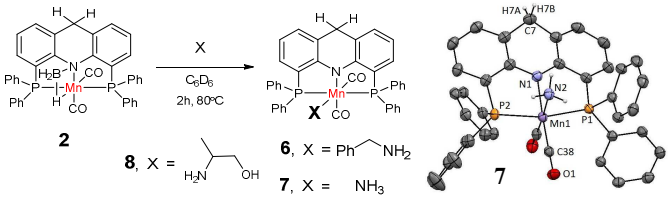
Dehydrogenation of the β-amino alcohol derivative catalyzed by **2** yields an aldehyde intermediate which undergoes self-coupling with another molecule, leading to 2,5-dihydropyrazine derivatives by elimination of 2 molecules of water. The 2,5-dihydropyrazine then undergoes rapid metal catalyzed dehydrogenation, 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. (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 (Scheme 4). Condensation with a second amine group leads to formation of a 1,2-dihydroquinoxaline derivative, which undergoes rapid dehydrogenation to form the quinoxaline derivative as the final product.



Scheme 4. Proposed mechanism for the dehydrogenative coupling reactions leading to pyrazine and quinoxaline formation

In order to gain further mechanistic insight, we tried to isolate possible active organometallic amido intermediates without the boron bridged moiety. The treatment of catalyst **2** with two equivalents 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 disappearance of the bound B*H* signal of complex **2** at –7.4 ppm 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 bridge BH_3 moiety was completely intact when complex **2** was treated with excess of NEt_3 or any primary alcohol. On the other hand, treatment of **2** with NH_3 (1 bar) the bridged BH_3 peaks 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 were observe 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 (Scheme 5). X-ray diffraction unambiguously showed a neutral octahedral ammonia coordinated manganese complex **7** bearing a hydrogenated acridine ring containing pincer ligand, 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 SI for the mechanism). Complexes **6** and **7** do not dehydrogenate the alcohol under neutral condition, whereas both the complexes are equally active compared to **2** for the pyrazine formation reaction in presence of catalytic amount of base. A toluene solution of 2-phenylglycinol was heated at 150°C for 24h in the presence of the isolated complex **7** (2 mol%) without any base in a close system afforded only 8% of the 2,5-diphenylpyrazine (amino group of 2-phenylglycinol act as a weak base, see next experiment) whereas addition of 3 mol% KH as base afforded 99% of the product under the same condition. Under the similar condition in presence of base and *in situ* generated complex **6** also showed the similar activity with 99% yield of the 2,5-diphenylpyrazine. Treatment of complex **2** with two equivalents 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. Addition of base to the reaction mixture and heating afforded the pyrazine derivative detected by GCMS. To obtain the active amido intermediate, complex **1** was treated with NaH in 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 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) which undergoes rapid reductive disproportionation to form a NMR silent compound. Reaction of complex **2** in presence 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 due to the less basic nature of the amido nitrogen of the ligand, alkoxide assisted alcohol dehydrogenation and dihydrogen liberation mechanism probably take place (see SI).



Scheme 5. Synthesis of complexes 6, 7 and 8

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 plau-

sibly proceeds by alcohol dehydrogenation followed by coupling with amines.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

Experimental procedure, crystal data of complexes 1, 2 and 7, GC-MS, NMR spectra of organic products are provided in supporting information. "This material is available free of charge via the Internet at http://pubs.acs.org."

ACKNOWLEDGMENT

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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