ChemPubSoc Europe
DOI: 10.1002/chem.201603148
CHEMISTRY
A European Journal
Communication

Pincer Complexes

Divergent Coupling of Alcohols and Amines Catalyzed by Isoelectronic Hydride Mn^{I} and Fe^{II} PNP Pincer Complexes

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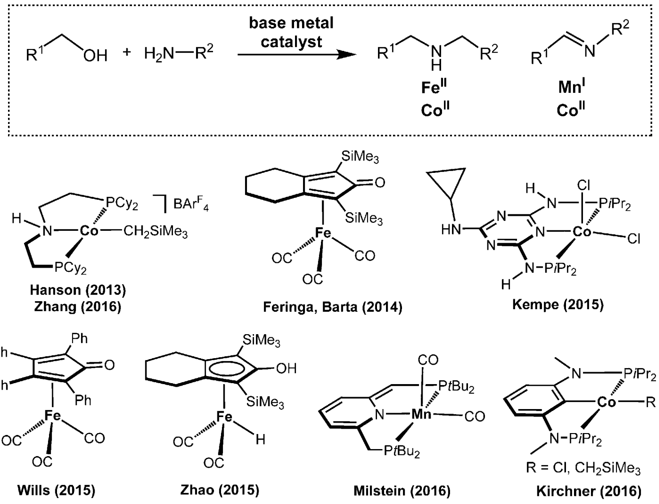
Abstract: Herein, we describe an efficient coupling of alcohols and amines catalyzed by well-defined isoelectronic hydride Mn^{I} and Fe^{II} complexes, which are stabilized by a PNP ligand based on the 2,6-diaminopyridine scaffold. This reaction is an environmentally benign process implementing inexpensive, earth-abundant non-precious metal catalysts, and is based on the acceptorless alcohol dehydrogenation concept. A range of alcohols and amines including both aromatic and aliphatic substrates were efficiently converted in good to excellent isolated yields. Although in the case of Mn selectively imines were obtained, with Fe—exclusively monoalkylated amines were formed. These reactions proceed under base-free conditions and required the addition of molecular sieves.

The catalytic coupling of amines with alcohols represents an environmentally benign and atom-economic pathway for the synthesis of substituted imines or amines that have important synthetic applications in the synthesis of dyes, fragrances, fungicides, pharmaceuticals, and agricultural chemicals.[1–3] In terms of sustainability, the choice of alcohols as substrates is highly desirable, because they are readily available by a variety of industrial processes and can be obtained renewably by fermentation or catalytic conversion of lignocellulosic biomass.[4] The catalytic cycle involves two or three successive steps: 1) acceptorless dehydrogenation (AD) of alcohols;[5] 2) imine formation; and 3) in situ hydrogenation of imines, provided that the hydrogen generated from the first step can be temporarily stored on the metal complex (borrowing hydrogen methodology). Key features are that the process is hydrogen neutral and that the only stoichiometric by-product is water and H_2 (in the case of imines).

Despite the significance of such coupling reactions, homogeneous catalysts mostly employ precious metals, such as Ru,[6] Rh,[7] Ir,[8] and Os.[9] In comparison, the same reaction with catalysts that utilize non-precious, earth-abundant metals[10] is much less developed although base metals demonstrated the ability to oxidize alcohols via AD.[11,12] Recently, Hanson and coworkers[13a] and Zhang and co-workers[13b] reported a Co catalyst, stabilized by a bis(phosphino)-amine (PNP) ligand (Scheme 1), which is able to give imines and/or amines depending on the reaction conditions. Kempe and co-workers described a new Co PNP pincer catalyst based on a triazine backbone, which was highly active for the alkylation of aromatic amines.[14] The groups of Feringa and Barta,[15a] Wills,[15b] and Zhao[15c] reported the alkylation of amines with alcohols to give amines by utilizing Fe catalysts featuring functionalized cyclopentadienone or hydroxycyclopentadienyl ligands based upon Knölker's complex or derivatives thereof.[16] We described



Scheme 1. Efficient base metal catalysts for the coupling of alcohols and amines involving acceptorless dehydrogenation of alcohols.

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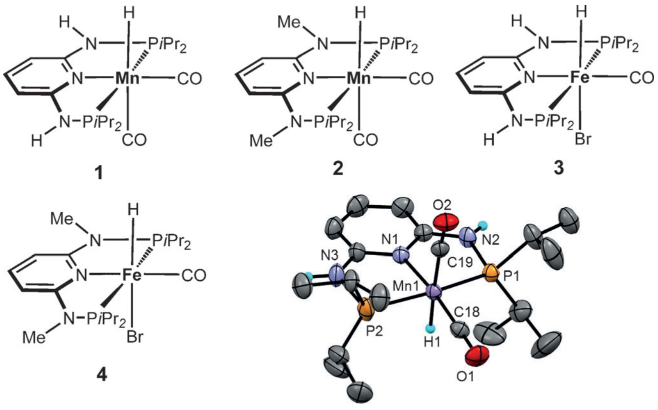
*Supporting information for this article and ORCIDs for some of the authors are available on the WWW under http://dx.doi.org/10.1002/chem.201603148. It contains complete crystallographic data, experimental details of the synthesis of all complexes including ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra, computational details, atomic coordinates of optimized species, and technical details in CIF format for **1** (CCDC 1479482 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre).*

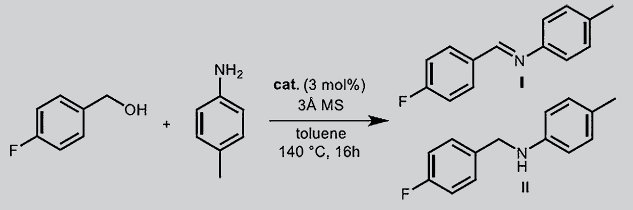
the application of well-defined Co^{II} catalysts, which feature a PCP ligand based on the 1,3-diaminobenzene scaffold.[17] Very recently, Milstein and co-workers[18] discovered the first Mn catalyst, which is active for the dehydrogenative coupling of alcohols and amines to form selectively imines. This catalyst features a deprotonated 2,6-bis-(di-*tert*-butylphosphino-methyl)pyridine pincer ligand. Noteworthy, this reaction does not require any additives, such as base or Lewis acids.

Intrigued by these recent discoveries, we describe herein the efficient coupling of alcohols and amines catalyzed by isoelectronic hydride Mn^{I} and Fe^{II} complexes, which are stabilized by a PNP ligand based on the 2,6-diaminopyridine scaffold. The aromatic pyridine ring and the phosphine $PiPr_2$ moieties are connected by NH or NMe linkers. The broad applicability of this ligand class has been demonstrated recently in the case of Fe, which are highly efficient catalysts for the hydrogenation of ketones, aldehydes and CO_2.[19] New Mn complexes **1** and **2** were synthesized, characterized, and applied in addition to the known Fe complexes **3** and **4**. The molecular structure of **1** was determined by X-ray crystal-structure analysis (Scheme 2).



Scheme 2. Mn and Fe complexes **1**–**4** tested as catalysts, and structural view of **1** showing 30 % thermal ellipsoids (most hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Mn1–P1 2.2074(7), Mn1–P2 2.2059(9), Mn1–N1 2.060(2), Mn1–C18 1.747(2), Mn1–C19 1.775(2), Mn1–H1 1.46(2); P1-Mn1-P2 161.00(3), N1-Mn1-C18 171.3(1), N1-Mn1-C19 96.2(1).

Table 1. Screening of Mn and Fe complexes as catalysts for the coupling of *p*-toluidine and 4-fluorobenzyl alcohol.[a]



Entry	Catalyst	Yield [%][b] I	Yield [%][b] II
1	**1**	84	
2	**2**		
3	**3**		81
4	**4**		
5[c]	**1**	39	
6[c]	**3**		14
7[d]	**3**	45	
8[d]	**1**		22
9[e]	**3**	41	19
10[f]	**1**	70	
11[f]	**3**		73

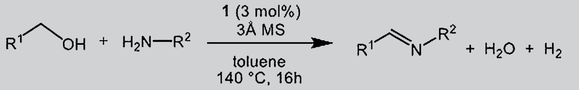
[a] Reaction conditions: 1.0 mmol 4-fluorobenzyl alcohol, 1.4 mmol *p*-toluidine, 0.3 g 3 Å MS, 3.0 mol % catalyst, 4 mL toluene, 140 °C, 16 h. [b] Isolated yields. [c] Without MS. [d] Without MS, 60 h. [e] Open system in *o*-xylene. [f] 1.0 mmol LiOTf.

First, the Mn and Fe catalysts **1**–**4** were screened for the coupling of 4-fluorbenzyl alcohol with *p*-toluidine (1.4 equiv) in toluene (4 mL) at 140 °C in a closed vial with added 3 Å molecular sieves (MS), and the results are summarized in Table 1. The products were analyzed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy and identified by comparison with authentic samples. In general, isolated yields after purification by column chromatography are reported. When **1** (3.0 mol % based on alcohol) was used as catalyst, selectively 1-(4-fluorophenyl)-*N*-(*p*-tolyl)methane imine (**I**) was obtained in 84 % yield (entry 1), whereas with **3**, the corresponding amine, *N*-(4-fluorobenzyl)-4-methylbenzene amine (**II**), was isolated in 81 % yield (entry 3). Catalysts **2** and **4** bearing NMe linkers were catalytically inactive, and no reaction took place (entries 2 and 4). This emphasizes the importance of the acidic NH moieties for the catalytic reaction. In the absence of MS, even after 60 hours, the yields were considerably lower (entries 5–8). When the reaction with **3** was performed in an open system, a mixture of imine and amine were obtained (entry 9). When the reaction was performed in the presence of LiOTf instead of MS, good yields were also achieved (entries 10 and 11) suggesting that Lewis acid property of these additives may also play a role.

Having established **1** and **3** as active catalysts, this methodology was applied to other substrates including benzyl alcohols and *n*BuOH, as well as aromatic and aliphatic amines. These results are shown in Tables 2 and 3. The resulting imines and *N*-alkylated amines were isolated in good to excellent yields. An exception is the Mn-catalyzed reaction of *n*BuOH and *p*-toluidine were only 17 % of the respective imine was obtained (Table 2, entry 6). The low yield was due to polymerization of the product under these reaction conditions. Moreover, in the case of Fe, exclusively monoalkylated amines were formed.

Simplified catalytic cycles with **1** and **3** as catalyst and precatalyst, respectively, are shown in Schemes 3 and 4. Key species are $\mathbf{A}^{Mn}$ and $\mathbf{A}^{Fe}$ with the latter being formed initially from **3** in the presence of base.[19c] Both compounds feature a deprotonated PNP ligand and are coordinatively unsaturated with the important difference that the first contains two, the latter only one inert CO co-ligand, but additionally a hydride ligand, which can participate in the catalytic reaction. Accordingly, the Fe system is capable of performing both alcohol dehydrogenation (oxidation cycle) and imine hydrogenation (reduction cycle) via an insertion mechanism. In the reduction cycle, coordination of dihydrogen ($\mathbf{E}^{Fe}$) and subsequent protonation of

Table 2. Dehydrogenative coupling of alcohols and amines to form imines utilizing catalyst **1**.[a]



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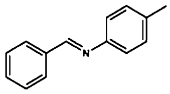
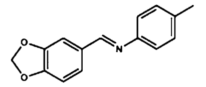
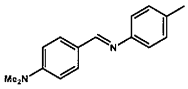
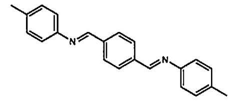
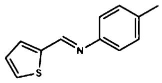
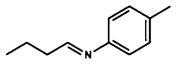
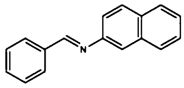
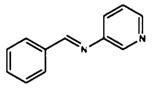
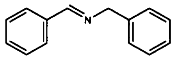
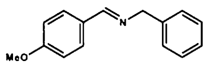
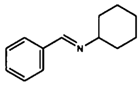
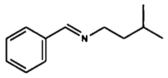
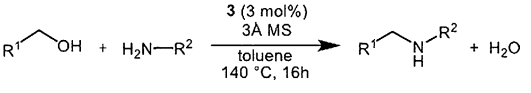
1		90 %	2		84 %
3		92 %	4		71 %
5		68 %	6		17 %
7		90 %	8		60 %
9		86 %	10		92 %
11		87 %	12		73 %

[a] Reaction conditions: 1.0 mmol alcohol, 1.4 mmol amine, 0.3 g 3 Å MS, 3.0 mol % catalyst, 4 mL toluene, 140 °C, 16 h. [b] Isolated yields.

Table 3. Coupling of alcohols and amines catalyzed by **3**.[a]



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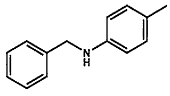
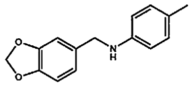
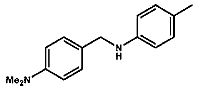
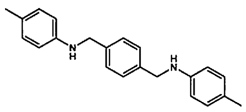
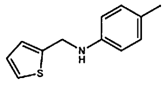
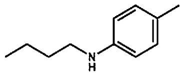
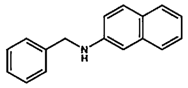
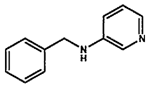
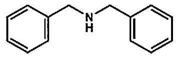
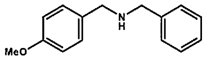
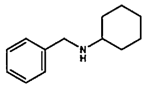
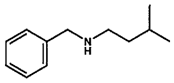
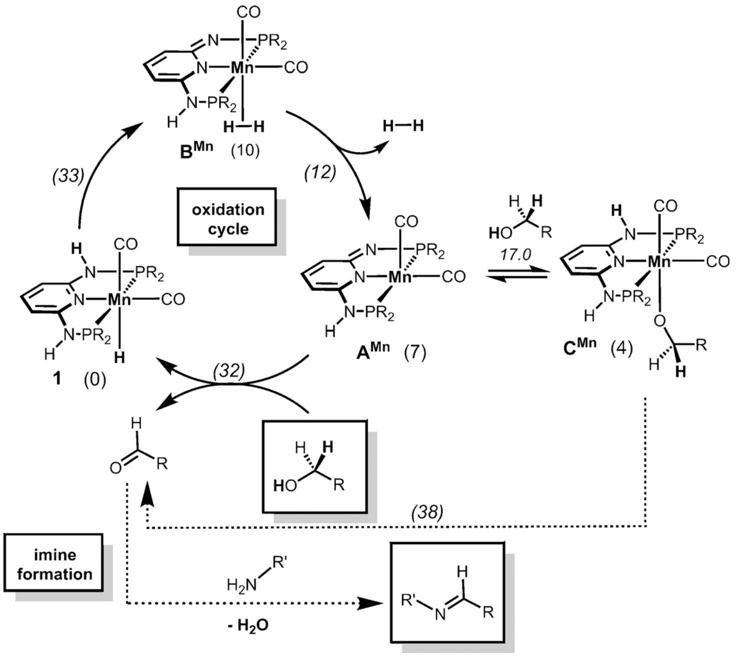
1		91 %	2		82 %
3		88 %	4		67 %
5		80 %	6		61 %
7		93 %	8		61 %
9		82 %	10		89 %
11		82 %	12		79 %

[a] Reaction conditions: 1.0 mmol alcohol, 1.4 mmol amine, 0.3 g 3 Å MS, 3.0 mol % catalyst, 4 mL toluene, 140 °C, 16 h. [b] Isolated yields.

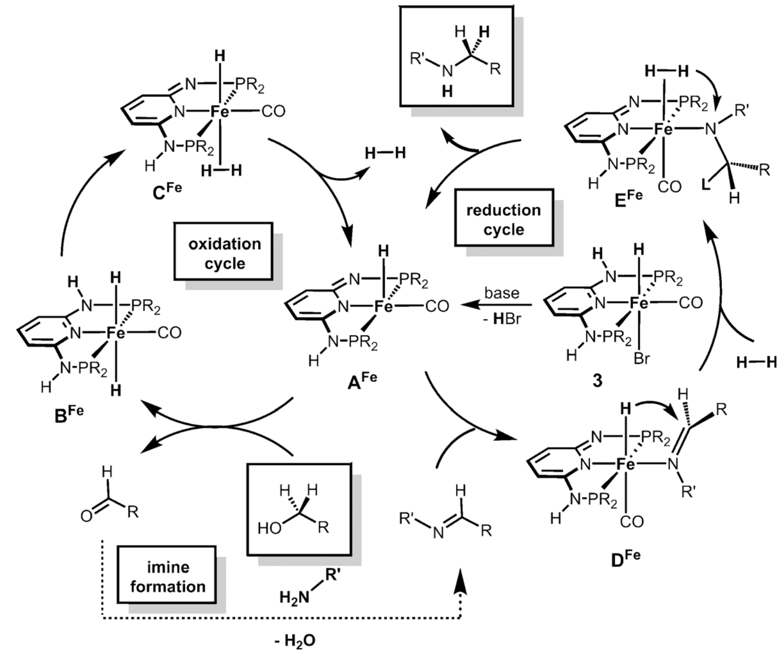
the imine N atom with formation of the amine and regeneration of the hydride (**A**^{Fe}) is essential. The same mechanism was recently proposed for the hydrogenation of ketones and aldehydes.[19c] The Mn system, on the other hand, is only able to oxidize the alcohol with concomitant irreversible H_2 release.

For the Mn-catalyzed reaction, we carried out preliminary DFT calculations[20] to establish a reasonable mechanism for the dehydrogenation of EtOH as model substrate. A summary of these results with the most relevant points along the catalytic cycle is presented in Scheme 3 (for details, see the Supporting Information). The first step is a proton transfer from the N atom of the PNP ligand to the hydride with formation of dihydrogen complex **B**^{Mn}. Hydrogen transfer is assisted by a nearby EtOH molecule acting as proton shuttle. This process is endergonic ($\Delta G=$ 10 kcal mol^{-1}) with the highest barrier $\Delta G^{\neq}$ along the path being 33 kcal mol^{-1}. In the next step, H_2 release from **B**^{Mn} gives the five-coordinate intermediate **A**^{Mn}. This occurs easily with a maximum barrier of 12 kcal mol^{-1} in an almost thermoneutral step. In the final step, an EtOH molecule approaches the metal center in outer-sphere fashion and protonates the PNP N atom regenerating **1** and releasing acetaldehyde. This process occurs in a single concerted step with a barrier of 32 kcal mol^{-1}. In a very recent work, a similar mechanism was proposed for the hydrogenation of nitriles with a related Mn PNP complex.[21]

The overall reaction has a high barrier of 33 kcal mol^{-1} in accordance with the experimental conditions, that is, reaction temperature of 140 °C, and a thermodynamically unfavorable free energy balance of 9 kcal mol^{-1}. Thus, the driving force must be provided by the consecutive reaction, that is, condensation between aldehyde and amine and probably by water re-



Scheme 3. Simplified catalytic cycle with **1** as catalyst. Free-energy values ([kcal mol^{-1}], barriers in italic) are referred to **1**.



Scheme 4. Simplified catalytic cycle with **3** as pre-catalyst.

moval by molecular sieves, as was indicated by the experimental observations.

Alternatively, dehydrogenation of EtOH may proceed via the ethoxide complex $\mathbf{C}^{\mathbf{Mn}}$, which undergoes β-elimination with regeneration of **1** and formation of aldehyde. However, this alternative pathway is less favorable than the one calculated for the concerted step.

In conclusion, we have reported two rare examples of an efficient coupling of alcohols and amines catalyzed by well-defined isoelectronic hydride Mn^{I} and Fe^{II} complexes, which are stabilized by a PNP ligand based on the 2,6-diaminopyridine scaffold. The precatalysts were easily prepared from commercially available reagents in a two-step procedure and in high yields. The coupling reactions are environmentally benign processes implementing inexpensive, earth-abundant non-precious metal catalysts and are based on the acceptorless alcohol dehydrogenation concept. A range of alcohols and amines including both aromatic and aliphatic substrates were efficiently converted in good to excellent isolated yields. In the case of Mn—selectively imines, and in the case of Fe—exclusively monoalkylated amines were formed. These reactions proceed under base-free conditions and required the addition of molecular sieves. Detailed mechanistic studies are currently underway. This work contributes to the development of waste-free sustainable base metal catalysis.

Acknowledgements

Financial support by the Austrian Science Fund (FWF) is gratefully acknowledged (Project No. P28866-N34), and L.F.V. acknowledges Fundação para a Ciência e Tecnologia, UID/QUI/00100/2013. The X-ray center of the Vienna University of Technology is acknowledged for financial support and for providing access to the single-crystal diffractometer.

Keywords: alcohols · amination · homogeneous catalysis · iron · manganese

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Received: July 1, 2016

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Pincer Complexes

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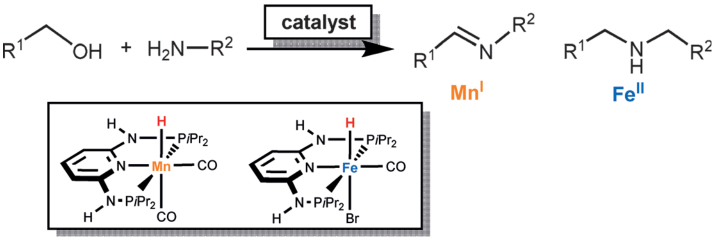
■■ – ■■

Divergent Coupling of Alcohols and Amines Catalyzed by Isoelectronic Hydride Mn^{I} and Fe^{II} PNP Pincer Complexes



Efficient coupling of alcohols and amines catalyzed by well-defined isoelectronic hydride Mn^{I} and Fe^{II} complexes is described. A range of alcohols and amines, including both aromatic and aliphatic substrates, was efficiently converted giving in the case of Mn selectively imines, whereas with Fe, exclusively amines were formed (see scheme).