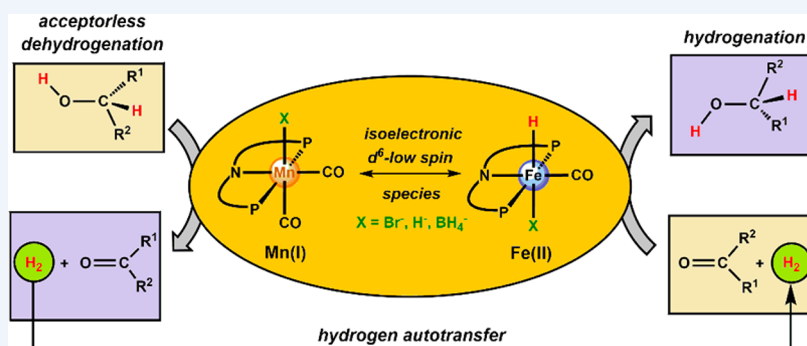


# Isoelectronic Manganese and Iron Hydrogenation/Dehydrogenation Catalysts: Similarities and Divergences

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**CONSPECTUS:** Sustainable processes that utilize nontoxic, readily available, and inexpensive starting materials for organic synthesis constitute a major objective in modern chemical research. In this context, it is highly important to perform reactions under catalytic conditions and to replace precious metal catalysts by earth-abundant nonprecious metal catalysts. In particular, iron and manganese are promising candidates, as these are among the most abundant metals in the earth's crust, are inexpensive, and exhibit a low environmental impact. As far as chemical processes are concerned, hydrogenations and acceptorless alcohol dehydrogenation (AAD), sometimes in conjunction with hydrogen autotransfer reactions, are becoming important areas of research. While the first is a very important synthetic process representing a highly atom-efficient and clean methodology, AAD is an oxidant-free, environmentally benign reaction where carbonyl compounds together with dihydrogen as a valuable product and/or reactant (autotransfer) and water are formed. Carbonyl compounds, typically generated in situ, can be converted into other useful organic materials such as amines, imines, or heterocycles.

In 2016 several groups, including ours, discovered for the first time the potential of hydride biscarbonyl Mn(I) complexes bearing strongly bound PNP pincer ligands or related tridentate ligands as highly effective and versatile catalysts for hydrogenation, transfer hydrogenation, and dehydrogenation reactions. These complexes are isoelectronic analogues of the respective hydride monocarbonyl Fe(II) PNP compounds and display similar reactivities but also quite divergent behavior depending on the coligands. Moreover, manganese compounds show improved long-term stability and high robustness toward harsh reaction conditions. In light of these recent achievements, this Account contrasts Mn(I) and Fe(II) PNP pincer catalysts, highlighting specific features that are connected to particular structural and electronic properties. It also addresses opportunities and restrictions in their catalytic applications. Apart from classical hydrogenations, it also covers the most recent developments of these catalysts for AAD resulting in the synthesis of complex organic molecules such as heterocycles via multicomponent reactions. The ambivalent hydrogen-based redox chemistry provides access to a variety of synthetically valuable reductive and oxidative coupling reactions. Hence, these catalysts cover a broad scope of catalytic applications and exhibit activities and productivities that are becoming competitive with those of well-established precious metal catalysts. The knowledge about the nature and characteristics of active Mn(I)- and Fe(II)-based systems paves the way for conceptually and mechanistically well-founded research, which might lead to further developments and the discovery of novel catalysts extending the current scope and limitations of reactivity. It underlines that base metal catalysts are beginning to challenge precious metal catalysts and contributes to the further advancement of waste-free sustainable base metal catalysis.

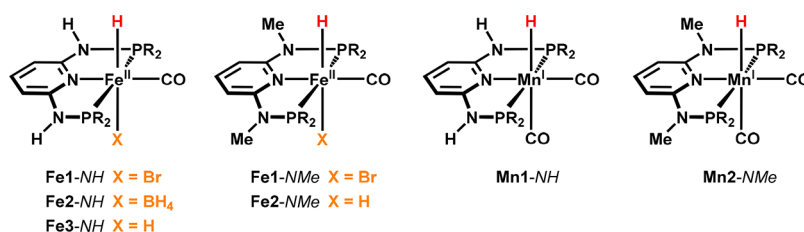
## INTRODUCTION

The development of sustainable, efficient, and selective syntheses is one of the fundamental research goals in modern chemistry. In this context, it is important to perform reactions under catalytic conditions and to replace precious metal catalysts by earth-abundant nonprecious metal catalysts.<sup>1</sup> As far as chemical processes are concerned, hydrogenations and acceptorless alcohol dehydrogenation, sometimes in conjunc-

tion with hydrogen autotransfer reactions, are becoming important areas of research.<sup>2,3</sup> In particular, iron and manganese constitute promising candidates, as these are among the most abundant metals in the earth's crust, are inexpensive, and exhibit a low environmental impact. While

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**Figure 1.** Well-defined Fe(II)- and Mn(I)-based catalysts developed by our group (R = *i*Pr).

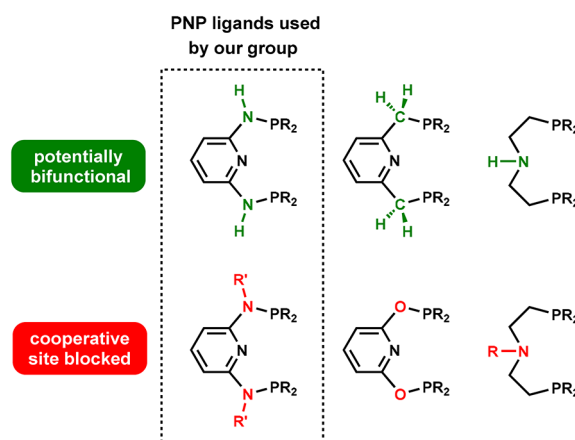
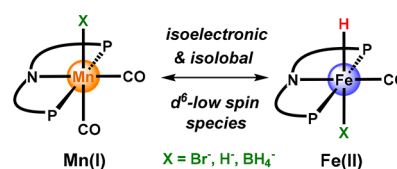
iron hydrogenation and dehydrogenation catalysts have been the subject of intense investigation over the past decade,<sup>4–8</sup> low-valent Mn(I) complexes just recently appeared as new but very powerful players in this field.<sup>9–12</sup> Concerning iron, the development of novel catalysts was largely inspired by concepts known from its well-established ruthenium congeners, which are particularly effective for hydrogenative reductions and oxidations of polar substrates. After the first reports on Fe(II)-catalyzed hydrogenations, we even stated “Iron, the New Ruthenium”.<sup>13</sup> However, in light of recent achievements accomplished by isoelectronic Mn(I) catalysts, the question arises whether this statement is still valid or has to be reconsidered, since these novel systems appear to show even more similarities to traditional ruthenium than iron chemistry (diagonal relationship Mn–Ru). Nevertheless, the development of base metal catalysts that can even compete with their “noble” analogues remains a challenging task since specific properties of first-row transition metals (e.g., oxidation states, spin states, ionic radii, redox potentials) are fundamentally different and new strategies and concepts have to be developed in order to circumvent unfavorable phenomena in this context. Consequently, the synthesis of isolated and structurally well-defined complexes combined with a fundamental understanding of reaction mechanisms appears to be a primary objective for the rational development of novel catalytic systems.<sup>14,15</sup>

In this Account, we describe well-defined Fe(II)- and Mn(I)-based catalysts featuring PNP pincer ligands based on 2,6-diaminopyridine that have been developed by our group (Figure 1).<sup>16–18</sup> We highlight common and characteristic features that influence the activity and selectivity of these systems and compare them with related PNP pincer systems. While Fe(II) and Mn(I) exhibit similar reactivities in many cases, these isoelectronic metal systems also reveal remarkable divergent behavior that will be emphasized in this contribution.

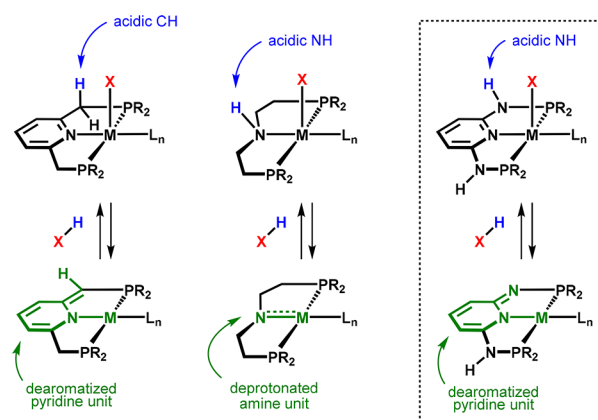
## ■ PNP PINCER LIGANDS: A VERSATILE PLATFORM FOR IRON AND MANGANESE CHEMISTRY

PNP pincer complexes proved to be particularly effective and versatile for hydrogenative reduction and dehydrogenative oxidation reactions of polar substrates,<sup>19</sup> where in many cases metal–ligand cooperation plays an important role (Figure 2).<sup>20</sup> Pincer complexes with aliphatic ligand backbones possess a secondary amine functionality adjacent to the metal center that is involved through an interplay between the amine/amide forms in H–H and H–heteroatom bond activation and formation steps. Lutidine-derived PNP pincers, on the other hand, are able to undergo reversible deprotonation of a methylene linker, which is accompanied by dearomatization of the heteroaromatic backbone (Figure 3).

In 2006, we started our research on transition metal PNP pincer complexes by focusing on a specific type of ligand in which the phosphorus donors are connected via NH or NR (R



**Figure 2.** Structural motifs of isoelectronic  $d^6$  low-spin Fe(II) and Mn(I) complexes featuring PNP pincer ligands.

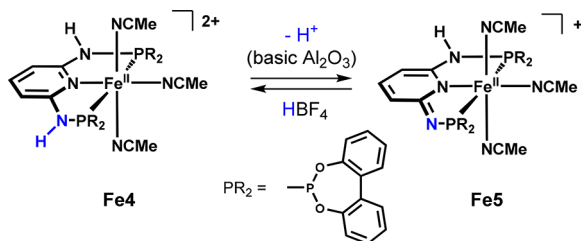


**Figure 3.** Metal–ligand cooperation in pyridine-based and aliphatic PNP pincer complexes.

= alkyl, aryl) linkers to a central pyridine unit.<sup>21</sup> These ligands, derived from the 2,6-diaminopyridine scaffold or derivatives thereof, are synthesized in a simple and modular fashion that allows access to a broad variety of structural, electronic, and stereochemical modifications. They show excellent chelating ability due to the strong donor groups, forming stable, rigid, and symmetric five-membered metallacycles, which also minimizes the occurrence of different isomers and facilitates spectroscopic characterization. These PNP pincer ligands thus

provide an excellent platform to explore base metal chemistry and catalysis, since they constitute an appropriate environment compensating for the intrinsically lower stability of 3d metals. Concerning metal–ligand cooperation, initial investigations revealed that a reversible aromatization/dearomatization reaction is feasible with this type of ligand. For example, the dicationic Fe(II) PNP complex **Fe4** affords the deprotonated complex **Fe5** in the presence of base (Scheme 1).<sup>19,21</sup>

**Scheme 1. Reversible Deprotonation of an NH Linker in Fe4**



Consequently, it appeared promising to explore the effect of NH and NR linkers in the backbone of pyridine-based PNP ligands in catalytic hydrogenations. However, in contrast to PNP ligands featuring CH<sub>2</sub> and O linkers, an advantage of PNP pincers based on 2,6-diaminopyridine is that cooperativity can be either blocked or activated by introducing substituents on the nitrogen linker. Such modifications contribute to the investigation of metal–ligand cooperation but also pave the way for the discovery of new reactivities and concepts. Accordingly, PNP systems based on aminopyridines benefit from both concepts mentioned above.

## ■ HYDROGENATION OF POLAR DOUBLE BONDS

The first results relevant for the development of our catalysts were obtained by demonstrating that our pincer complexes are capable of activating molecular hydrogen in a bifunctional manner (Scheme 2).<sup>22</sup> The biscarbonyl complex *trans*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>Cl]<sup>+</sup> (**Fe6**) reacts with Zn as a reducing agent under a dihydrogen atmosphere to give the Fe(II) hydride complex *cis*-[Fe(PNP-*i*Pr)(CO)<sub>2</sub>H]<sup>+</sup> (**Fe7**). The crucial step in this reaction is the reduction of the acidic NH protons of the PNP ligand to afford H<sub>2</sub> and the coordinatively unsaturated intermediate [Fe(PNP<sup>H</sup>-*i*Pr)(CO)<sub>2</sub>] bearing a dearomatized/deprotonated pyridine moiety. This species is able to bind and

heterolytically cleave H<sub>2</sub> to give **Fe7**. However, this hydride complex is catalytically inactive, indicating that bifunctionality is not the only requirement for an active system (vide infra).

Inspired by the seminal work of Milstein and co-workers,<sup>23,24</sup> we focused on [Fe(PNP-*i*Pr)(H)(CO)(Br)] (**Fe1-NH**), which incorporates a bromide instead of a second carbonyl ligand *trans* to the hydride. In contrast to the cationic biscarbonyl iron hydride complex tested before, **Fe1-NH** was an effective hydrogenation catalyst capable of reducing ketones and aldehydes under mild conditions (Scheme 3).<sup>25</sup> A structural view of **Fe1-NH** is depicted in Figure 4.

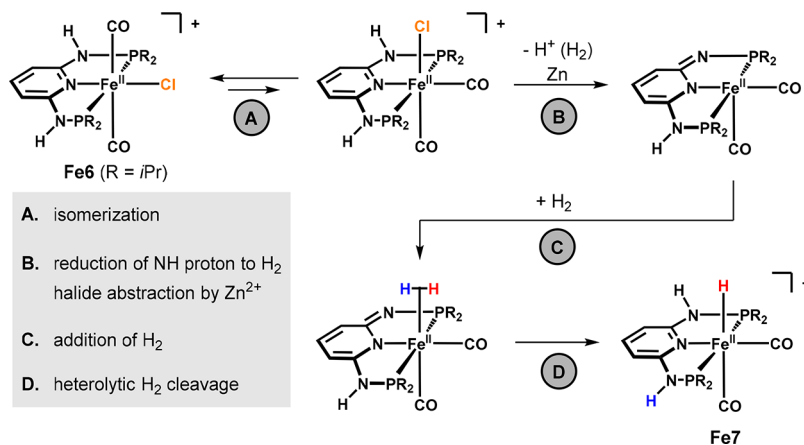
Although the catalytic performance was not enhanced in comparison to related catalysts,<sup>23,24</sup> this system paved the way for systematic variations that provided valuable information on the structural requirements for obtaining a catalytically active complex. It turned out that the bromide *trans* to the hydride is substitutionally labile and is readily replaced by anionic or neutral coligands, resulting in a series of different hydride complexes (Scheme 4).

Treatment of **Fe1-NMe** with H<sub>2</sub> in the presence of a strong base readily yields a mixture of *trans*- and *cis*-**Fe3-NMe** (Scheme 5). These complexes could even be structurally characterized by X-ray crystallography (Figure 4). In the case of **Fe1-NH** featuring acidic NH linkers, the analogous dihydrides are also formed in solution, but they could not be isolated in the solid state.

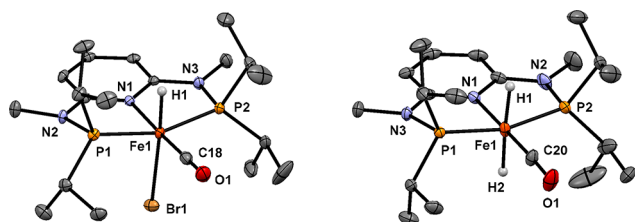
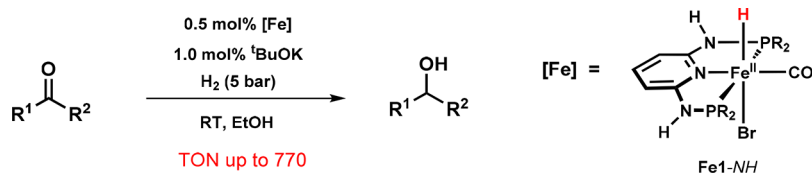
Initial screening of these complexes in the hydrogenation of acetophenone revealed that only complexes with labile coligands are catalytically active, indicating that the formation of a vacant coordination site is required. Moreover, we investigated the role of metal–ligand cooperation by modifying the substituents on the nitrogen linkers. Accordingly, only **Fe1-NH** featuring acidic NH groups could hydrogenate ketones, while **Fe1-NMe** bearing NMe linkers was catalytically inactive.

On the basis of these findings, a catalytic cycle is proposed (Scheme 6). The deprotonated intermediate **A1** is the catalytically active species and is thought to be stabilized by the reversible addition of the solvent alcohol to give the reprotonated hydride alkoxide complex **F1**. Since **A1** represents a formal 16-electron complex, providing a free coordination site for an incoming substrate, the mechanism is considered to proceed via coordination of the ketone prior to its insertion into the metal hydride bond. In principle, two different pathways for the release of the product alcohol and the

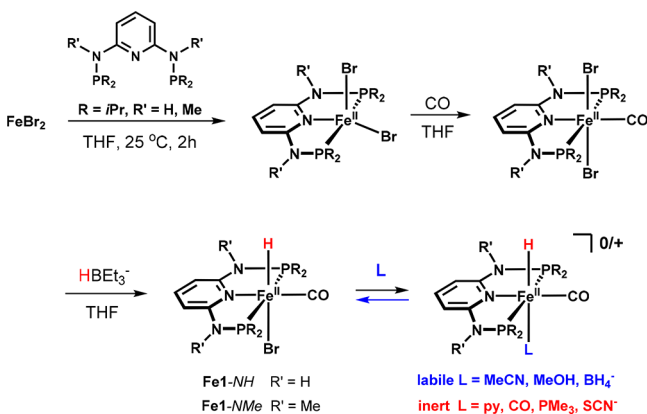
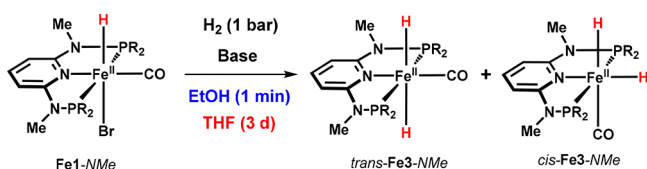
**Scheme 2. Heterolytic Cleavage of H<sub>2</sub>**



## Scheme 3. Iron-Catalyzed Hydrogenation of Ketones and Aldehydes

Figure 4. Structural views of Fe1-NH and *trans*-Fe3-NMe.

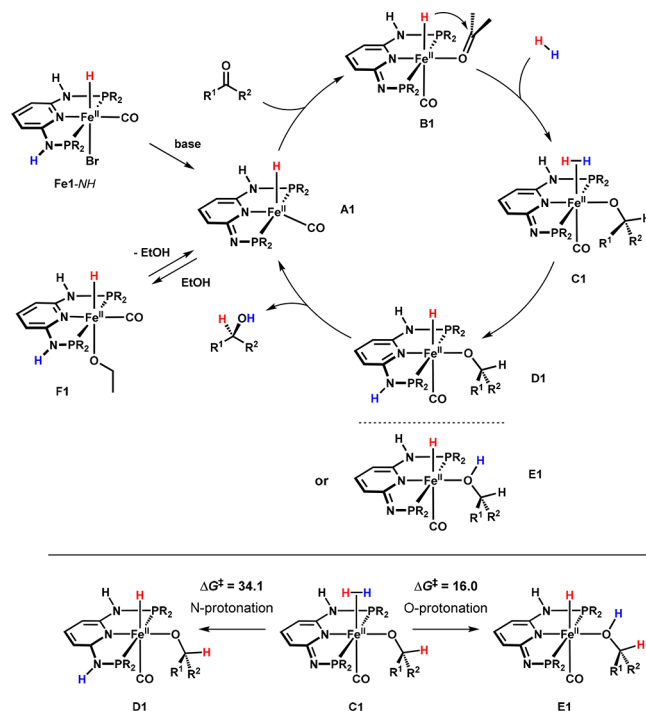
## Scheme 4. Preparation of Iron Hydride Complexes Featuring Labile and Inert Coligands

Scheme 5. Synthesis of *cis*- and *trans*-Fe3-NMe

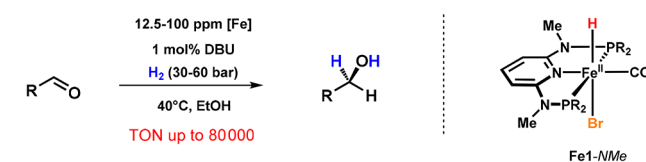
regeneration the initial intermediate A1 were considered to be feasible. Either dihydrogen is activated by aromatization of the ligand followed by elimination of the product (D1), which again leads to a dearomatized system, or H<sub>2</sub> is directly cleaved between the iron center and the product alkoxide without reprotonation of the nitrogen linker (E1). DFT calculations showed that the latter pathway is energetically more favorable, indicating that deprotonation of the NH linker is not involved in the heterolytic cleavage of H<sub>2</sub> but instead is necessary for catalyst activation by generating a vacant coordination site and by increasing the negative charge at the metal center.

It was thus quite surprising that under the same conditions Fe1-NMe, which is unable to promote the reduction of ketones, was found to catalyze the hydrogenation of aldehydes in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base (Scheme 7).<sup>26</sup> Moreover, this system not only provides complete chemoselectivity for aldehydes over ketones and other reducible functional groups but exhibits extremely high activity and productivity. A variety of different aromatic,

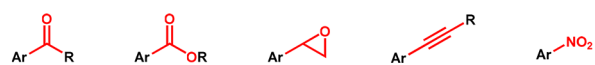
## Scheme 6. DFT-Calculated Mechanism of the Iron-Catalyzed Hydrogenation of Ketones and Aldehydes



## Scheme 7. Chemoselective Hydrogenation of Aldehydes

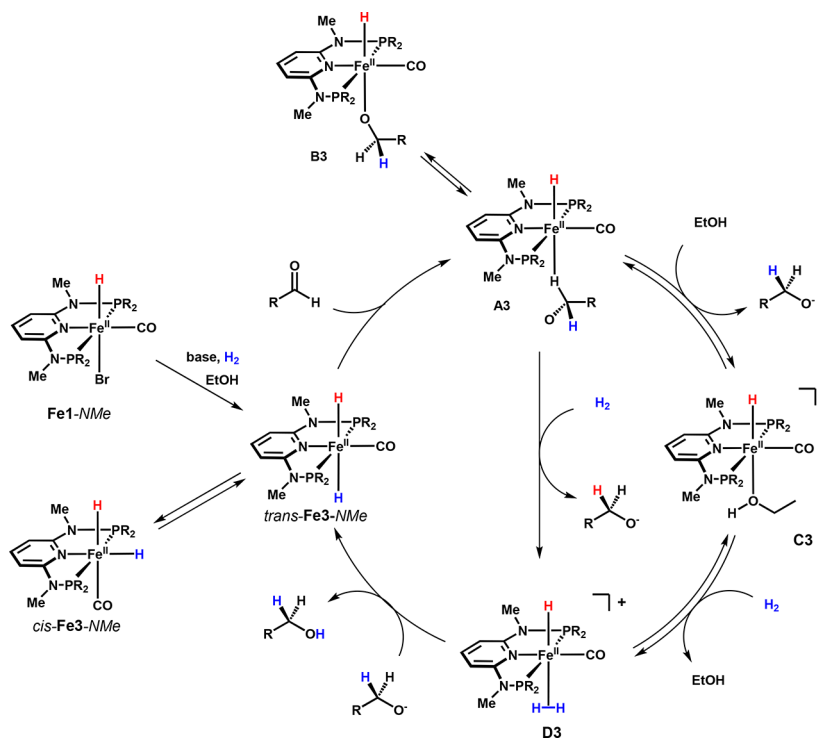


substrates that are not hydrogenated:



heteroaromatic, and aliphatic aldehydes could be quantitatively converted into the corresponding primary alcohols, reaching turnover numbers (TONs) of up to 80 000, which are among the highest reported for an iron-based hydrogenation catalyst. In contrast to the hydrogenation of ketones catalyzed by Fe1-NH, an iron dihydride was identified as key intermediate. A catalytic cycle is depicted in Scheme 8. The precatalyst Fe1-NMe readily forms a mixture of complexes *trans*- and *cis*-Fe3-NMe as a result of heterolytic cleavage of dihydrogen promoted by the iron center and the external base. Substrate insertion proceeds through an outer-sphere mechanism in which the nucleophilic dihydride directly attacks the aldehyde's carbonyl group to give intermediate A3 featuring a H-coordinated alkoxide, which is in equilibrium with B3 where the alkoxide is



Scheme 8. Hydrogenation of Aldehydes Catalyzed by *trans*-Fe3-NMe

O-coordinated. Replacement of the alkoxide either by the solvent (ethanol) or dihydrogen leads to the formation of C3 or D3, respectively. The latter features an  $\eta^2$ -bound dihydrogen ligand. Subsequent deprotonation of the coordinated  $H_2$  finally leads to the regeneration of *trans*-Fe3-NMe and liberation of the product. Complexes B3 and C3 could be detected by NMR spectroscopy in stoichiometric experiments. DFT calculations revealed that the alkoxide complex B3 represents a resting state outside the catalytic cycle. This reasonably explains why the catalytic reaction proceeds only in protic solvents, which permit catalytic turnovers by solvent-assisted release of the alkoxide. The remarkable substrate selectivity, i.e., aldehydes versus ketones, was recently explained by the relative stability of alkoxide intermediates formed upon aldehyde insertion into an Fe–H bond of *trans*-Fe3-NMe based on state-of-the-art DFT calculations.<sup>27</sup>

In light of the exceptional catalytic performance and the industrial relevance of the chemoselective reduction of aldehydes, we also focused on the immobilization of Fe1-NMe. Since direct immobilization of a sensitive homogeneous catalyst on a solid support often results in partial or complete loss of activity because the active species suffers from a modification of its chemical and physical properties, an alternative and more convenient approach was chosen by preparing a supported ionic-liquid-phase (SILP) catalyst.<sup>28</sup>

For this purpose, Fe1-NMe was dissolved in an ionic liquid (IL) and impregnated on a porous support (Figure 5). Gratifyingly, the chemical nature of the catalyst was preserved, yet the catalyst was dissolved in a separate phase that was easily separated from the reaction solution. This novel SILP system was successfully applied to the chemoselective hydrogenation of aromatic and aliphatic aldehydes to give alcohols under mild conditions (0.1–0.05 mol % catalyst, 25 °C, 50 bar  $H_2$ ) without leaching of the catalyst. Although immobilization leads to decreased catalytic activity compared with the analogous

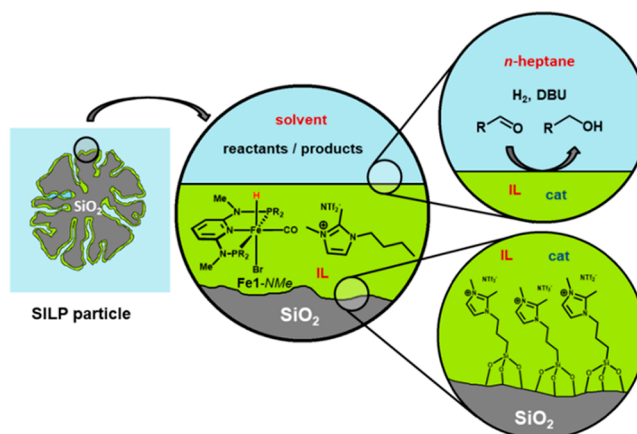


Figure 5. Iron–SILP system as a precatalyst for the chemoselective hydrogenation of aldehydes.

homogeneous hydrogenation, it was possible to perform recharge experiments by adding additional substrate to the reaction mixture before the end of the reaction, showing that the new SILP system continuously catalyzes the reaction and making it interesting for applications under continuous flow conditions.

On the basis of the knowledge about the factors that affect the reactivity of our iron complexes, we realized striking similarities when manganese hydrogenation and dehydrogenation catalysts were first reported.<sup>29–33</sup> Since complex Fe7 was found to be catalytically inactive, it was surprising to find that the isostructural and isoelectronic complex Mn1 is a highly reactive species.

This difference essentially arises from the higher electron density around manganese in the +I oxidation state, which also has a large influence on the reactivity of the M–H bond. As revealed by DFT calculations, the M–H distances as well as

charge distributions in Mn(I) hydride complexes are very similar to those found in the respective Fe(II) dihydride species (Figure 6).<sup>34</sup>

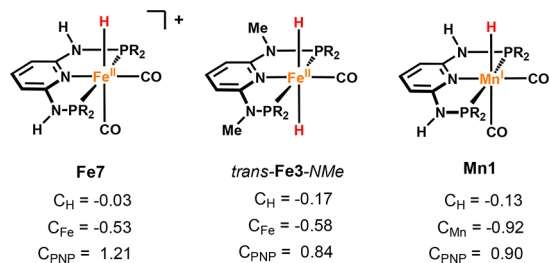


Figure 6. NPA charges of Fe(II) and Mn(I) PNP complexes.

An analysis of the frontier orbitals of the dearomatized species of **Fe1-NH** and **Mn1-NH** reveals that Fe(II) hydrido carbonyl and Mn(I) biscarbonyl PNP complexes are isolobal to each other. Both systems are able to promote H–H and H–heteroatom bond-breaking and -making reactions, with the metal center being acidic (LUMO) and the linker (HOMO) being basic (Figure 7). The HOMO corresponds to the ligand  $\pi$  system, with a significant contribution of the lone pair of the deprotonated N atoms (basic site). The LUMO is essentially the metal  $d_z^2$  orbital pointing toward the empty coordination position (acidic site).

The Mn(I) PNP hydride complexes **Mn1-NH** and **Mn1-NMe** were prepared by treating  $Mn(CO)_2Br$  with 1 equiv of the PNP ligand to yield complexes of the types  $[Mn(PNP)(CO)_2Br]$  (**Mn11-NH**) and/or  $[Mn(PNP)(CO)_3]Br$  (**Mn12**) depending on the amine linker. Both complexes react with  $[HBt_3]^-$  to afford the hydride complexes **Mn1-NH** and **Mn1-NMe**, respectively (Scheme 9).

In the same way as the iron dihydride complex *trans*-Fe3-NMe, the monohydride **Mn1-NH** was found to be a highly active catalyst for the hydrogenation of aldehydes, while other reducible functionalities including ketones, carboxyl acid derivatives, and C=C double bonds remained unaffected (Scheme 10).<sup>35</sup> **Mn1-NMe** was completely inactive, emphasizing the importance of the acidic NH linkers in enabling a bifunctional mechanism. In contrast to **Fe1-NMe**, which requires the presence of an external base for the activation of  $H_2$ , **Mn1-NH** can be used under base-free conditions since hydrogen is cleaved in an intramolecular fashion by cooperation of the metal center and the deprotonated nitrogen linker

(bifunctional catalysis). It has to be noted that related Mn(I) PNP pincer complexes were shown to act as catalysts for the hydrogenation of ketones and aldehydes but required higher catalyst loadings (0.1–5.0 mol %), higher temperatures (80–130 °C), and 1–10 mol % base (KO<sup>t</sup>Bu) in toluene as the solvent.<sup>36,37</sup>

Apart from carbonyl compounds, we investigated the application of these catalysts to the hydrogenation of  $CO_2$ .<sup>38</sup> Both the complexes bearing NH linkers and those containing NMe linkers were found to promote the catalytic hydrogenation of  $CO_2$  and  $NaHCO_3$  to formates (Scheme 11). NMR and DFT studies highlight the role of dihydride and hydride complexes in the catalytic process. The mechanism strongly resembles the one previously proposed for the selective hydrogenation of aldehydes, since insertion of  $CO_2$  into the metal–hydride bond was also found to proceed via a nucleophilic attack in the outer coordination sphere of the catalyst. It has to be mentioned that **Fe1-NH** was inactive in EtOH, since the formation of the respective dihydride is effectively suppressed in this solvent (Scheme 12). However, reasonable catalytic activity was found for the hydrogenation of formate when the reaction was carried out in THF/water mixtures. On the other hand, with **Fe1-NMe** the best results for the hydrogenation of  $CO_2$  were observed by using EtOH as the solvent in the presence of stoichiometric amounts of DBU, reaching TONs of more than 10 000 and high yields of formate.

With **Mn1-NH** we reported the first example of Mn(I)-catalyzed hydrogenation of  $CO_2$  to give HCOOH (Scheme 13).<sup>38</sup> The catalytic performance of this system is quite similar to that of the iron dihydride complex *trans*-Fe3-NMe, reaching TONs of up to 10 000, and quantitative yields were obtained after 24 h using DBU as the base at 80 °C and a total pressure of 80 bar. **Mn1-NH** showed improved long-term stability under the applied reaction conditions. In contrast to iron, we could accomplish a significant increase of the reaction rate by employing lithium triflate as a cocatalyst,<sup>39–41</sup> yielding TONs of more than 30 000, which are among the highest reported for base-metal-catalyzed  $CO_2$  hydrogenations to date.

Analogously to our mechanistic studies on iron, we recognized that nucleophilic attack of the hydride on  $CO_2$  in the second coordination sphere of the metal constitutes the key step of the reaction. Moreover, this step leading to the formation of the corresponding formate species constitutes a convenient model illustrating the basicity of the hydride complex. Accordingly, we could compare the natures of the M–H bonds in these Fe(II) and Mn(I) hydride complexes by

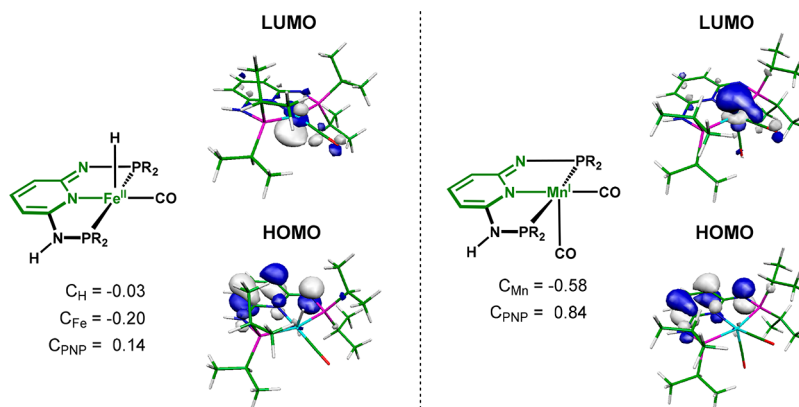
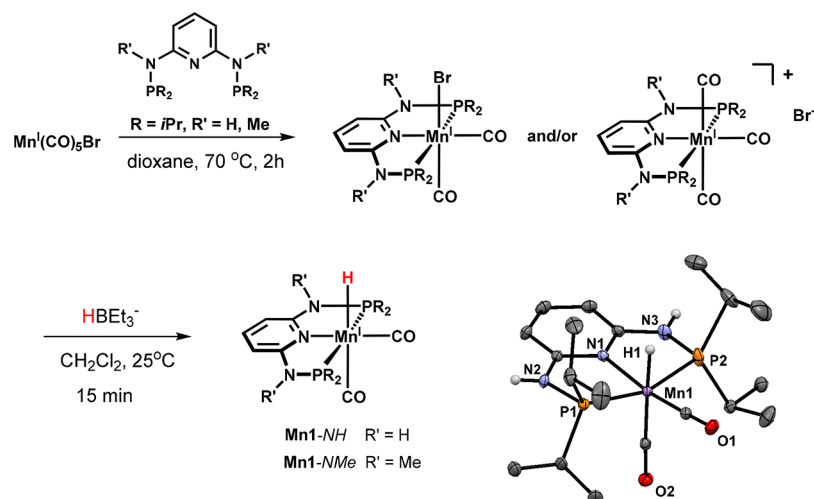
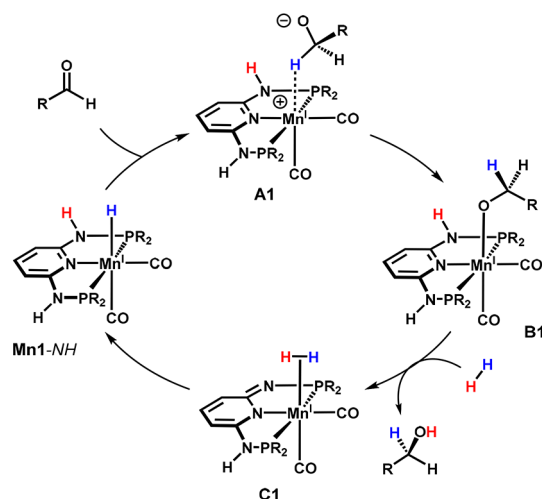
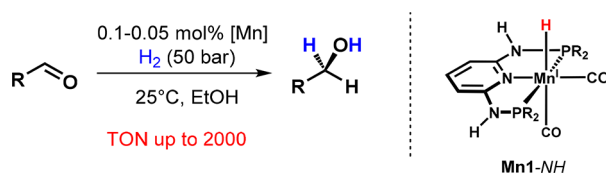
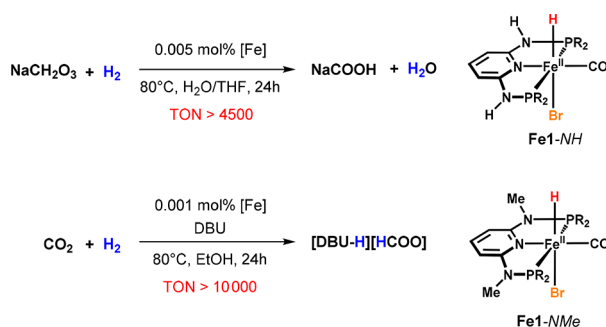


Figure 7. LUMOs and HOMOs of dearomatized Fe(II) and Mn(I) PNP complexes.

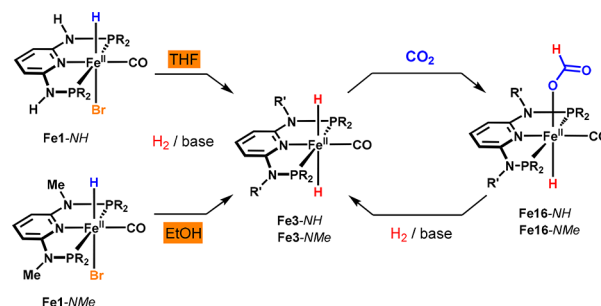
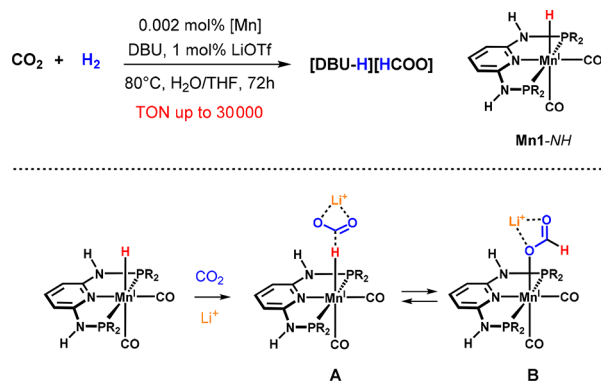
Scheme 9. Synthesis of Mn1-NH and Mn1-NMe (Structural View of Mn1-NH)



Scheme 10. Chemoselective Manganese-Catalyzed Hydrogenation of Aldehydes

Scheme 11. Iron-Catalyzed Hydrogenation of CO<sub>2</sub> and NaHCO<sub>3</sub>

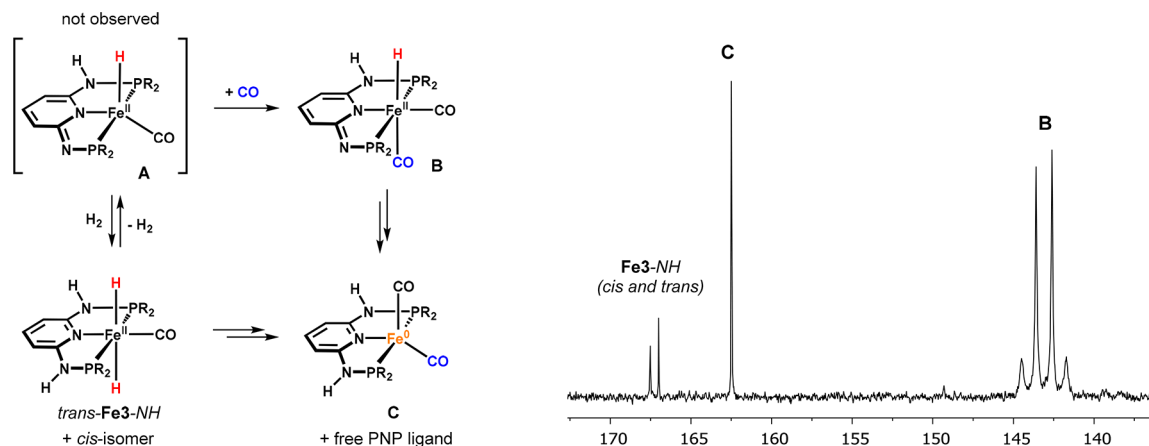
means of DFT calculations. These data also show that insertion into the metal–hydride bond is thermodynamically unfavorable

Scheme 12. Formation of Fe3-NH and Fe3-NMe and Reaction with CO<sub>2</sub>Scheme 13. Manganese-Catalyzed Hydrogenation of CO<sub>2</sub>

in the case of Mn1-NMe featuring NMe linkers. In fact, this catalyst displayed only poor catalytic activity. Finally, the beneficial effect of LiOTf might be related to the stabilization of the  $\kappa^1$ -H-bound formate in A, since B represents a resting state that is outside the catalytic cycle.

## ACCEPTORLESS ALCOHOL DEHYDROGENATION AND HYDROGEN AUTOTRANSFER REACTIONS

Our results obtained from hydrogenation reactions nicely illustrated the similarities between iron and manganese and substantially contributed our knowledge about the main factors that influence the basic reactivities of these catalysts. However, an aspect that appears to be at least equally important for further catalytic applications is the reversibility of these

Scheme 14. Trapping of B and Detection by  $^{31}\text{P}\{^1\text{H}\}$  NMR Spectroscopy

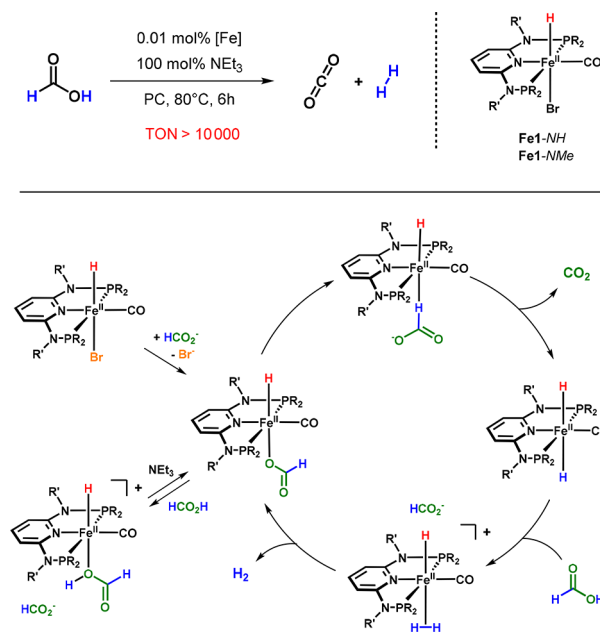
processes. Therefore, as the formally reverse process, we also focused on dehydrogenation reactions, which in contrast to hydrogenations unveiled significant differences between iron and manganese.

While iron complexes supported by aliphatic PNP pincer ligands were shown to catalyze not only the hydrogenation of unsaturated compounds but also the acceptorless dehydrogenation of saturated substrates,<sup>42,43</sup> pyridine-based systems have not yet been found to promote such a reaction. This difference may be attributed to the fact that unsaturated 16-electron intermediates formed in the course of  $\text{H}_2$  liberation via metal–ligand cooperation are efficiently stabilized by the deprotonated nitrogen atom, which acts as both a strong  $\sigma$  and  $\pi$  donor. In contrast, pyridine-based pincer systems are only weak  $\pi$  donors and thus are unable to stabilize 16-electron intermediates (Figure 7). Accordingly, complexes with aliphatic PNP amido ligands could even be isolated and structurally characterized.<sup>39,43</sup> The deprotonated 16-electron species A in the case of Fe1-NH could not be observed directly but could be trapped in the presence of CO in the form of  $[\text{Fe}(\text{PNP}^{\text{H}}-i\text{Pr})(\text{H})(\text{CO})_2]$  (B), which exhibits a characteristic AB pattern in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (Scheme 14). Together with B, the formation of the Fe(0) complex  $[\text{Fe}(\text{PNP}-i\text{Pr})(\text{CO})_2]$  (C),<sup>22</sup> free PNP ligand, and intractable materials were also observed. Scrambling of the CO ligands to form C represents a major decomposition and catalyst deactivation pathway.

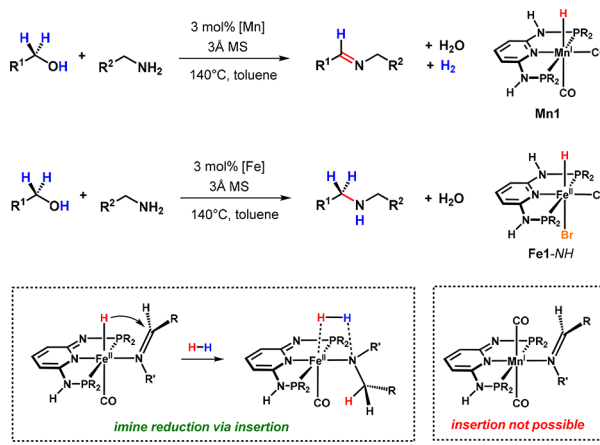
Dehydrogenation of formic acid, which was found to be catalyzed by the iron complexes Fe1-NH and Fe1-NMe, constitutes the only exception, since this reaction, just as the hydrogenation of  $\text{CO}_2$  mentioned before, does not proceed via a bifunctional mechanism (Scheme 15).<sup>44</sup>

In contrast to iron, manganese PNP pincer complexes are much more suitable for acceptorless dehydrogenations, particularly considering dehydrogenative coupling reactions. For example, we found that Mn1 is able to promote the catalytic coupling of alcohols and amines to yield imines, thereby generating water and molecular hydrogen as the sole byproducts (Scheme 16).<sup>45</sup> For comparison, we also tested the iron complex Fe1-NH in this reaction. Surprisingly, this complex was catalytically active as well but afforded secondary amines instead. It has to be mentioned that this divergent reactivity between the Fe and Mn catalysts is a particular property of pyridine-derived PNP complexes. While Milstein and co-workers also reported on the dehydrogenative coupling of alcohols and amines catalyzed by a lutidine-based system,<sup>29</sup>

Scheme 15. Iron-Catalyzed Dehydrogenation of Formic Acid



Scheme 16. Coupling of Alcohols and Amines Catalyzed by Mn(I) and Fe(II) PNP Pincer Complexes



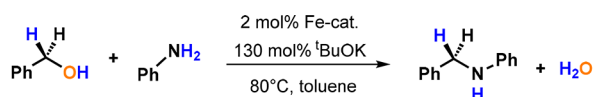
Mn catalysts based on aliphatic PNP pincer ligands were found to promote coupling reactions that proceed via a hydrogen autotransfer mechanism and do not liberate dihydrogen.<sup>46–48</sup>



Mechanistic consideration suggests that in both cases the O–H bond of the alcohol is cleaved between the metal center and the deprotonated side arm of the ligand to form an alkoxide intermediate, which is converted to the respective aldehyde via a nonclassical  $\beta$ -hydride elimination. The resulting hydride and dihydride complexes, respectively, release dihydrogen in a bifunctional manner, recovering the initial deprotonated 16-electron species again. However, while Mn just reenters this catalytic cycle, it seems obvious that iron allows for the insertion of the imine that has been formed by condensation of the aldehyde and an amine to finally yield an amine in the presence of the previously released  $H_2$ . This separate reduction cycle proceeds analogously to the mechanism that we proposed for the hydrogenation of ketones. Moreover, it gives a reasonable explanation for the divergence between the two metals, as Mn is not capable of following an insertion pathway.

We recently also discovered that instead of the rather sensitive catalyst **Fe1-NH**, even the respective iron dibromide PNP complexes and related triazine-based dibromide complexes, which are more easily accessible and air-stable, can be used as precatalysts for the alkylation of amines with alcohols.<sup>49</sup> Systematic variations of the ligand scaffold can be accomplished, giving valuable information on structure–activity relationships (Scheme 17).

**Scheme 17.** Alkylation of Amines with Alcohols Catalyzed by Air-Stable Precatalysts

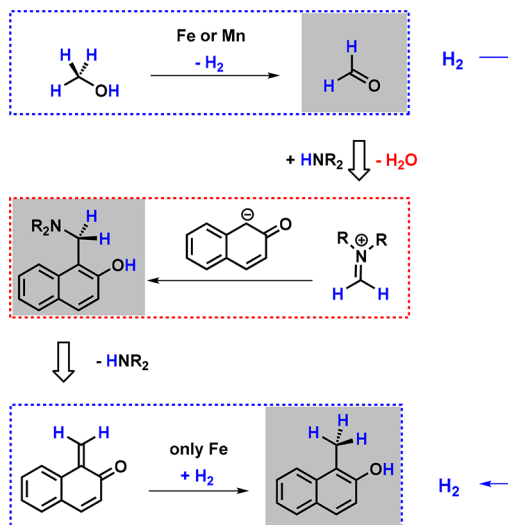


entry	X	Y	R'	yield (%)
1	NH	C	H	84
2	NMe	C	H	0
3	CH <sub>2</sub>	C	H	24
4	NH	N	Me	80
5	NH	N	Ph	51
6	NH	N	NMe <sub>2</sub>	91

Divergence was also observed when **Mn1-NH** was applied for the catalytic aminomethylation of phenols and hetero-aromatic compounds utilizing amines and MeOH as a C1 building block (Scheme 18).<sup>50</sup> From a mechanistic perspective, this represents a Mannich-type reaction requiring formaldehyde as a reactant, which is generated in situ through the catalytic

dehydrogenation of MeOH. In a preliminary study, **Fe1-NH** was shown to catalyze the methylation of 2-naphthol rather than its aminomethylation, underlining the divergent reactivity of isoelectronic Mn(I) and Fe(II) PNP pincer systems (Scheme 19).

**Scheme 19.** Simplified Mechanism of the Mn- and Fe-Catalyzed Aminomethylation of 2-Naphthol

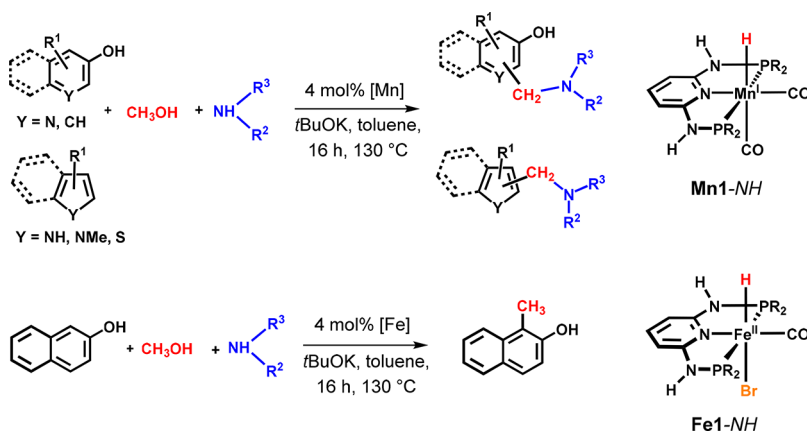


Finally, the ability of Mn(I) PNP complexes to promote a sequence of dehydrogenation and condensation steps that gives rise to selective C–C and C–N bond formations could even be extended to more complex structures. For example, **Mn1-NH** was successfully employed in the synthesis of substituted quinolones and pyrimidines using combinations of 2-amino-benzyl alcohols and alcohols as well as benzamidine and two different alcohols, respectively (Scheme 20).<sup>51</sup> The Kempe group even extended this concept to pyrroles and tetrasubstituted pyrimidines by using analogous triazine-based catalysts.<sup>52,53</sup>

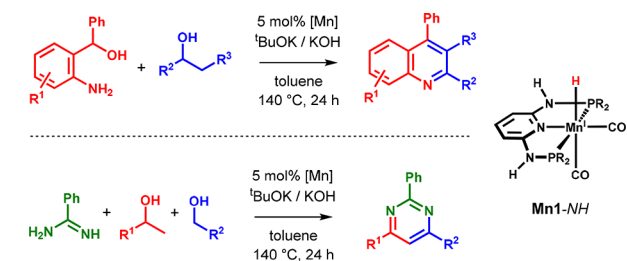
## SUMMARY AND OUTLOOK

We have described the catalytic activity of well-defined isoelectronic Fe(II) and Mn(I) PNP pincer complexes based on the 2,6-diaminopyridine scaffold or derivatives thereof that have been developed in our group. Several of these compounds

**Scheme 18.** Manganese-Catalyzed Aminomethylation of Aromatic Compounds



### Scheme 20. Manganese-Catalyzed Multicomponent Reactions To Yield Quinolines and Pyrimidines



are active catalysts for the hydrogenation of carbonyl compounds as well as for the acceptorless dehydrogenation of alcohols. The key aspects of these catalysts have been the recognition of decisive structural features, i.e., enabling and blocking of bifunctional behavior by variations of the amine linkers (NH vs NR) as well as the determination and optimization of proper reaction conditions that permit high catalytic turnovers. Mechanistic insights, including catalyst activation and the identification of the reactive species, revealed specific similarities and differences between the described systems. The current knowledge about the nature and characteristics of active iron- and manganese-based systems has paved the way for conceptually and mechanistically well-founded research that may lead to further developments and the discovery of novel catalysts extending the scope and limitations of reactivity. One aspect is the replacement of CO by other  $\pi$ -accepting ligands such as  $\text{NO}^+$ ,  $\text{CN}^-$ , or isocyanides or the partial or complete removal of CO ligands, which may provide new reactivities as already accomplished with Fe(II) polyhydride complexes, e.g.,  $[\text{Fe}(\text{PNP}^{\text{Me}}\text{-iPr})(\text{H})_2(\eta^2\text{-H}_2)]$ .<sup>54</sup> Challenging in Mn(I) chemistry also will be the development of catalysts that originate from inexpensive Mn(II) materials, as Mn(I) catalyst formation is currently restricted to the expensive precursor  $[\text{Mn}(\text{CO})_5\text{X}]$  (X = Cl, Br). In view of the many inspiring discoveries and achievements in homogeneous manganese and iron catalysis in the past few years, it seems that research into this field is merely at the beginning of its development and that many breakthroughs are still ahead, rewarding those who do not mind great challenges.

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#### Notes

The authors declare no competing financial interest.

#### Biographies

**Nikolaus Gorgas** (born in 1987 in Vienna, Austria) received his M.S. degree in 2012 from the University of Vienna, working with Prof. Walter Weissensteiner. Afterward he joined the research group of Prof. Karl Kirchner at the Technical University of Vienna (TU Wien), where he obtained his Ph.D. in 2017. He is currently a postdoctoral fellow in the same group. His present research interests include base metal polyhydrides and  $\sigma$ -bond complexes and their applications in homogeneous catalysis.

**Karl Kirchner** (born in 1960 in Wiener Neustadt, Austria) obtained his diploma (1984) and his doctoral degree (1987) from TU Wien, working with Prof. Roland Schmid. After a two-year postdoctoral stay at Washington State University with Prof. John P. Hunt and an additional postdoctoral year with Nobel Laureate Prof. Henry Taube at Stanford University, he returned to TU Wien and completed his Habilitation with Prof. Roland Schmid (1994). He is presently Professor of Organometallic Chemistry and Head of the Division of Inorganic Chemistry. His expertise is centered around the themes of ligand design, synthesis of well-defined nonprecious transition metal complexes, and their applications in homogeneous catalysis.

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