First-Row Transition Metal (De)hydrogenation Catalysis based on Functional Pincer Ligands

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ABSTRACT: The use of 3d metals in de-/hydrogenation catalysis has emerged as a competitive field with respect to ‘traditional’ precious metal catalyzed transformations. The introduction of functional pincer ligands that can store protons and/or electrons as expressed by metal-ligand cooperativity and ligand redox-activity strongly stimulated this development as conceptual starting point for rational catalyst design. This reviews aims at providing a comprehensive picture of the utilization of functional pincer ligands in first-row transition metal hydrogenation and dehydrogenation catalysis and related synthetic concepts relying on these such as the hydrogen borrowing methodology. Particular emphasis is put on the implementation and relevance of cooperating and redox-active pincer ligands within the mechanistic scenarios.

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1 INTRODUCTION

First-row transition metal compounds have emerged in recent years as homogeneous catalysts for numerous organic transformations,^{1–19} such as de-/hydrogenation,^{18,20–33} and other hydroelementation^{34–38} reactions that were traditionally the realm of precious metal catalysis. The development of base metal hydrogenation catalysts also inspired sustainable concepts for the controlled release and fixation of dihydrogen within chemical energy storage schemes.^{32,39–46} Due to the generally lower toxicity compared with 4d and 5d metal complexes,⁴⁷ the use of 3d metals is less environmentally harmful meeting several principles of Green Chemistry. Furthermore, 3d metals are considerably more abundant in the continental crust than their heavier 4d/5d homologues, ranging from scandium (16 ppm) to iron (43200 ppm), the fourth most abundant element (Figure 1).⁴⁸ In contrast, some 4d metals (Ru, Rh, Pd) and most of the 5d metals (in particular Re, Os, Ir and Pt) are rare elements with limited deposits suitable for today's mining technology.

VI	VII	VIII	IX	X	XI
Cr 126	Mn 716	Fe 43200	Co 24	Ni 56	Cu 25
Mo 1.1	Tc	Ru 0.0001	Rh 6·10 ⁻⁵	Pd 0.0004	Ag 0.07
W 1.0	Re 0.0004	Os 5·10 ⁻⁵	Ir 5·10 ⁻⁵	Pt 0.0004	Au 0.0025

Figure 1. Abundance of mid to late transition metals in the earth's continental crust (concentration in ppm).⁴⁸

The increasing demand and cost for noble metal precursors sparked a rising interest in their replacement for more abundant homogeneous catalysts. However, the robustness (expressed in the *turnover number* TON) and the activity (expressed in the *turnover frequency* TOF) of base metal catalysts often lacks behind the performance of noble metal catalysts. The emergence of base metal catalysis was therefore strongly driven by the development of sophisticated ligand systems as an enabling methodology. The proportional cost of such complex ligand platforms for 3d metal catalysis with high activity and selectivity, should not be underestimated. Besides cost considerations, the field of base metal catalysis is therefore also driven by catalytic transformations that have not been realized with precious metal catalysts before.

'Pincer' ligands were introduced by Shaw in 1976.⁴⁹ According to the early definition by van Koten and Albrecht, pincer ligands are tridentate ligands with a central, σ -donating phenyl moiety that carries two lateral amino- or phosphinomethyl CH_2ER_2 ($\text{E} = \text{N}, \text{P}$) side groups in *ortho*-position.⁵⁰ As a result of the chelating, rigid binding mode, transition metal complexes often exhibit high thermal stability and well defined reactivity at the remaining coordination sites, which has been extensively exploited in catalysis and

many other application.^{2,32,51–60} However, the term 'pincer ligand' has since been considerably widened to a point where a precise definition is blurred by the inclusion of many meridionally binding, mono-, di- and tri-anionic and even neutral tridentate ligands that cover a vast range of central and flanking coordinating groups and 'backbones' linkers connecting them. This structural and electronic variability allows for versatile fine-tuning of chemical properties, which strongly contributed to the success of the pincer ligand and concept.^{54,61–64} Importantly, the conceptual utilization of functional pincer ligands decisively stimulated base metal catalyzed de-/hydrogenation catalysis.

Scheme 1. Schematic representations of typical hydrogenation cycles of olefins and carbonyl groups with and without formal metal redox changes.^{65,81}

The parameters that contribute to the activity of 3d metal hydrogenation catalysts with respect to their heavier homologues were recently discussed by Zell and Langer.⁶⁵ Within a strongly simplified picture, two 'conventional' mechanistic scenarios are well established for hydrogenation of olefins and carbonyl groups, respectively (Scheme 1): The dihydride mechanisms (right) imply substrate binding, stepwise hydrogen transfer to the substrate and H_2 oxidative addition, associated with formal metal ± 2 redox steps. Within monohydride mechanism (left), metal redox events are avoided by H_2 heterolysis with proton transfer from a dihydrogen ligand to alkyl (olefin hydrogenation) or alkoxy (carbonyl hydrogenation) ligands. These considerations define the relevant parameters that determine the thermochemical framework for comparing 3d vs 4/5d metal catalysts, i.e. (1) substrate binding constants (2) $\text{M}-\text{H}$ vs. $\text{M}-\text{C}/\text{O}$ bond strength as expressed by bond dissociation free energies (BDFE) for homolytic processes and $\text{M}-\text{H}$ hydricity (ΔG_{H^-}) and pK_a for hydride or proton transfer, respectively, and (3) acidity of the dihydrogen intermediate as expressed by $\text{pK}_a(\text{M}-\text{H}_2)$.^{66–68} These parameters will be discussed in the next sections in the context of two ligand design principles that have been instrumental in the emergence of first-row

metal catalysis, i.e. the introduction of redox active pincer ligands^{27,69–74,78,142–145} and metal-ligand cooperativity.^{26,27,30,32,39,46,51,77,93}

This review aims at covering the application of functional pincer ligands in 3d metal catalyzed de-/hydrogenation. The term ‘functional ligand’ has been used for a variety of different phenomena of active ligand participation both in the first and second coordination sphere around the metal.⁷⁸ Within this review on de-/hydrogenation catalysis we will focus on redox active and cooperating pincer ligands to discuss the relevance of reversible reservoirs for protons and/or electrons in pivotal organic applications of proton coupled electron transfer. Both principles have been separately reviewed.^{26,27,30,32,39,46,51,69–74,77,78,93,142–145} However, the direct comparison offers additional insights for catalyst design.

Scheme 2. Simplified, schematic representations of redox-active, cooperating and chemically non-innocent pincer ligands.²⁰³

1.1. Metal-ligand Cooperativity (MLC)

As a general trend, first row transition metal hydrides exhibit slightly lower M–H BDFEs compared with analogous heavier analogues by approximately 5–10 kcal mol^{−1}.^{79,80} Furthermore, exchange of ligands, such as CO for phosphines or phosphites had negligible effects on the M–H BDFE within error. As judged from the rather limited body of systematic data, first row transition metal hydride BDFEs seem to be at the lower end for what is required for H₂ (BDFE_{MeCN} = 102 kcal mol^{−1}) oxidative addition. From these considerations, first-row catalysts seem generally less suitable to engage in hydrogenation cycles that proceed through H₂ oxidative addition (Scheme 1).

Ionic hydrogenation that relies on H₂ heterolysis provides an alternative mechanistic scenario.⁸¹ H₂ activation and transfer along such a pathway is thermochemically defined by M–H acidities (pK_a) and hydricities (ΔG_{H−}). The most comprehensive body of experimental pK_a data for metal hydride and dihydrogen complexes was compiled for group 8 compounds, yet with limited examples for full Fe/Ru/Os-series

in identical coordination environment. No clear trend along the group could be found, but the pK_a differences between iron and ruthenium are generally small within 1–2 units while osmium compounds are less acidic accounting for stronger 5d M–H bonding.⁶⁷ In fact, Morris’ increment methods for estimating M–H acidities does not discriminate between first- and second-row metals.⁸²

M–H hydricities have a strong dependence on the metal and ligand sphere. Within a homologous M^{II}H(diphosphine)₂⁺ group 10 series, the nickel compound exhibited considerably higher hydricity in the order ΔG_{H−}(Ni) >> ΔG_{H−}(Pt) > ΔG_{H−}(Pd) by more than 40 kcal mol^{−1}, which renders nickel(II) by far the weakest hydride donor.⁸³ The same general trend is observed for example for M^{III}H₂(diphosphine)₂⁺ and M^IH(diphosphine)₂ (M = Co, Rh),^{84–87} or computed hydricity values for MH(CO)₅ (M = Mn, Re; ΔΔG_{H−} = 11 kcal mol^{−1}).⁸⁸ Kubiak and co-workers recently showed for a broad range of 3–5d transition metal hydrides that the hydricities (ΔΔG_{H−} ≈ 45 kcal mol^{−1}) exhibit a decent linear correlation with the one-electron reduction of the metal complexes in their respective hydride acceptor form (E°([M]/[M][−])).⁸⁹ From a thermochemical cycle, hydricity ΔG_{H−}⁰ can be expressed as a function of M–H BDFE and the free energies for reduction of the complex E°([M]/[M][−]) and the free hydrogen atom (ΔG_{H/H−}⁰):

$$\Delta G_{H-}^0 = \text{BDFE}_{M-H} + nFE^\circ([M]/[M]^-) + \Delta G_{H/H-}^0 \quad (1)$$

The approximately linear correlation suggests that the variation in BDFE is comparatively small vs. the impact of the redox potential on hydricity. Strong hydride donor species will therefore be obtained for low complex charges and metal oxidation states and strongly σ-donating ligands (hydrides, alkylphosphines). Such ligands in labilizing *trans*-position to the hydride will further reduce the M–H BDFE and therefore increase the hydricity. Corresponding trends were found for Ru ketone hydrogenation catalysts.^{90,91} From these consideration, strong-field pincer ligands seem to be a good choice due to the strong σ-donating ability. Furthermore, the stereochemical rigidity of pincer ligands enables to direct other strong-field ligands in *trans*-position to the catalytically relevant site. For example, a *trans*-dihydride configuration is generally found for active iron pincer catalyst species in de-/hydrogenation of polar substrates, which is discussed in section 3.

The development of hydrogenation catalysts for polar multiple bonds and particularly the conceptual transfer to first-row metal catalysis were strongly driven by the introduction of functional ligands that can serve as proton relays to facilitate H₂ heterolysis (Scheme 2). An early, classical example in precious metal catalysis is Shvo’s catalyst which carries a proton responsive cyclopentadienone ligand.⁹² This structural and functional motif could be transferred to iron catalysis by Knölker.⁴ Seminal contributions were made by Noyori’s group reporting bisphosphine ruthenium catalysts with primary diamine ligands that exhibited extraordinary activities, chemoselectivities for C=O over C=C (transfer) hydrogenation and stereoselectivities.^{93,94} An ‘NH-effect’

was confirmed by a dramatic drop in activity in the absence of N–H groups. It was originally attributed to cooperative H₂ cleavage by the metal and a deprotonated amide ligand leading to an amine hydride complex with *syn*-configuration. Concerted hydride and proton transfer to the substrate without pre-coordination to the metal center was proposed as next step, to account for the high chemoselectivities and stereoselection.^{93,95–101} However, stepwise outer-sphere mechanisms were more recently discussed as alternative scenarios challenging the direct involvement of an amide intermediate in catalysis.¹⁰²

Figure 2. Exemplary outer-sphere processes of cooperating pincer ligands in de/hydrogenation catalysis.¹⁰³

Several terms are used to describe the involvement of the auxiliary ligands in these reductive transformations. For Noyori's amine catalysts and systems inspired by them, *bifunctional catalysis* and Grützmacher's definition of *metal-ligand cooperativity* (MLC) are commonly applied, which requires ligands that *actively participate in substrate activation* and facilitate catalysis *with the metal ion in a synergistic way*.¹⁰⁴ Within a more narrow definition metal and ligand undergo *reversible chemical modifications* in this process, such as ligand deprotonation/ reprotonation.^{105,106} As pointed out by Dub and Gordon, cooperating ligands can also contribute to rate acceleration in ionic hydrogenation cycles without synergistic metal/ligand substrate activation, such as substrate polarization or outer-sphere stabilization of reduced substrate anions via hydrogen bonding (Figure 2).¹⁰³ They therefore propose to reserve the term *bifunctional catalysis* for synergistic metal/ligand scenarios. We will here apply Milstein's widespread definition for MLC-assisted mechanisms,¹⁰⁶ which includes reversible chemical steps at the ligand to distinguish them from alternative pathways that are often compared from computational evaluation. However, we want to emphasize the argument of Dub and Gordon that the role of these ligands in catalysis can be subtle and often offer different catalytic pathways that are close in energy.

Figure 3. Privileged metal-ligand cooperating pincer platforms in first-row de-/hydrogenation catalysis.

Over the last two decades several pincer platforms were introduced with excellent performance as privileged cooperating ligands in de/hydrogenation catalysis (Figure 3).¹⁰⁶ The aliphatic PN^HP ‘aminopincer’ framework resembles structural features of Noyori's original catalysts and was also extensively utilized in first-row metal catalyzed de-/hydrogenation. In comparison to the pyridine- and triazine-based privileged ligands, the ligand backbone exhibits a high degree of flexibility, contrary to the original definition of pincer ligand.

Scheme 3. Proposed, MLC-assisted pathway for iron catalyzed ketone hydrogenation.¹⁰⁷

A major advance in the field of MLC-assisted catalysis was made by the Milstein group upon introduction of pyridine-based pincer ligand PN^PP (Figure 3).^{51,107,109,110} Versatile synthetic access to this ligand platform strongly contributed to its widespread use. Deprotonation of a methylene group in the backbone produces an anionic, ‘dearomatized’ pincer ligand with amide character. Such dearomatized complexes can undergo stoichiometric, cooperative H₂ heterolysis by 1,3-addition across the metal-ligand framework. This de-/aromatization reactivity is often anticipated to be relevant for catalysis (Scheme 3). However, non-MLC-assisted pathways are also frequently encountered in de-/hydrogenation catalysis as discussed in the respective sections. Kirchner's PN₃P and the triazine-based PN₅P pincer ligands (Figure 3) represent variants with more acidic and rigid secondary amine groups in the backbone.^{110,111}

Scheme 4. H₂ 1,6-addition across a quinone-based PCP pincer iron(II) complex **Fe-2a** and use for alkyne semihydrogenation (P = PiPr₂).¹¹²

The application of these MLC-ligands had a tremendous effect on the advancement of first-row metal catalysis, particularly with Mn, Fe and Co.^{20,21,25,26,30,46,113,114} Related pincer scaffolds were introduced that rely on alternative modes of ligand cooperativity. For example, a redox-active, carbenoid metallaquinone pincer ligand was reported, which undergoes long-range metal-ligand H₂ 1,6-addition to form a ferrihydroquinone (Scheme 4).¹¹² The reversible process

allows for stoichiometric hydrogenation of alkynes and the compound was used for alcohol oxidation to aldehydes.¹¹²

Scheme 5. Stoichiometric, MLC-assisted H₂-activation facilitated by functional PPP and PCP pincer ligands.^{115–119}

A rapidly growing structural and functional variety of cooperating pincer ligands with many different cooperating groups were subjected to stoichiometric bond activation reactions and some proved suitable for catalysis. For example, Thomas and coworkers described the 1,2-addition of dihydrogen across a covalent Co-P bond (Scheme 5).¹¹⁵ Gutsulyak et al. reported 1,2-addition of E-H bonds (E = H, NH₂, OH, OCH₃, CCPh, NHC(O)Ph, SiPh₃) at a nickel carbene PCP pincer complex,^{116–119} and Caulton and coworkers the 1,2-addition of dihydrogen along the Ni-N moiety of a cationic amido pincer Ni(II) complex (Scheme 6).¹²⁰ The bimetallic Ni(I)/Ni(I) PBP pincer complex **Ni-6a** was reported by Peters to undergo reversible MLC-assisted addition of dihydrogen (Scheme 6) but is inactive in olefin hydrogenation.¹²¹

Scheme 6. Stoichiometric, MLC-assisted H₂-activation facilitated by functional PNP and PBP pincer ligands.^{120,121}

1.2. Redox Active Ligands

The coordination and organometallic chemistry of 3d vs. 4f/5d metals exhibits some critical differences with respect to (electronic) structure that strongly impact catalysis.^{15,70,104,122–127} For example, coordinatively unsaturated iron complexes are much more frequent than for ruthenium owing to the stability of tetrahedral high-spin iron(II) in

weak ligand fields.⁶⁵ However, substrate binding to tetrahedral h.s.-Fe^{II} requires considerable conformational rearrangement, which imposes an energetic penalty. Furthermore, spin pairing is usually a prerequisite to sufficiently activate a weakly binding substrate like H₂. For example, transient ³Fe(CO)₄ exhibits drastically lowered rates towards H₂ oxidative addition in comparison with ¹Ru(CO)₄.^{128,129} For iron, the ('spin-forbidden') reaction proceeds on two different spin surfaces. Spin-orbit coupling mixes the pure spin states in the region of surface crossing allowing for transition. However, in case of weak spin-orbit coupling ($\zeta(\text{Fe}^{3+}) = 460 \text{ cm}^{-1}$, $\zeta(\text{Ru}^{3+}) \approx 1250 \text{ cm}^{-1}$, $\zeta(\text{Os}^{3+}) \approx 3000 \text{ cm}^{-1}$)¹³⁰ and strong distortion in the crossing region, an additional kinetic barrier with low transmission probability may arise.^{131,132} The implications of these aspects on substrate binding are further exemplified by the diffusion dynamics of the 16-electron species ³Fe(CO)₄ vs. ¹Cr(CO)₅ in hydrocarbon solvents, which is considerably slower for the singlet compound due to alkane coordination.¹³³ From these considerations, *rigid strong-field ligands*, such as diphosphino pinners, that avoid trapping of active first-row catalysts in unproductive high-spin states should be beneficial for hydrogenation catalysis.^{15,54,70,122–124} However, *redox-active weak-field pincer ligands* (see below) provide an alternative approach.¹²⁶ Notably, open-shell first-row catalysts proved instrumental in C–C coupling¹²⁵ and multi-state reactivity that crosses through low-lying spin surfaces along the reaction coordinate can accelerate catalytic transformations, which further complicates predictions.^{134,135}

Figure 4. Schematic electronic configurations of (**Ph₂PPrPDI**)Mn¹³⁶ and (**PDI**)FeN₂.¹³⁷

Redox-active ligands exhibit low lying electron donor or acceptor levels that result in distinctly ligand based redox events upon oxidation or reduction of respective metal complexes (Scheme 2). Ambiguous oxidation state assignments can arise in case of close energetic proximity of ligand and metal based frontier orbitals.^{137,138} Jørgensen coined the term redox non-innocence for cases where an accurate electron count within the metal valence shell is not possible.¹³⁹ The terms redox-activity and (non-)innocence are frequently used in the same context and sometimes even synonymously, but should be distinguished to avoid confusion.^{127,140} For example, ligand non-innocence not necessarily refers to ligand-based radicals as implied by redox activity. Oxidation state ambiguity can also occur in closed shell systems, such as (**PDI**)Fe(CO)₂ or (**PDI**)Fe(N₂)₂ (**PDI** = pyridinediimine ligand) which can be described as {(**PDI**)²⁻

Fe^{II} or $\{(\text{PDI})\text{Fe}^0\}$.^{137,141–143} The recent advances in modern spectroscopic tools and quantum-chemical electronic structure methods have strongly contributed to enable precise redox state assignments based on physical observables.

First-row transition metal ions with weak field ligands have a higher tendency to adopt high or intermediate spin states, such as $(\text{Ph}_2\text{PPrPDI})\text{MnCl}_2$,¹³⁶ $(\text{PDI})\text{FeCl}_2$,¹⁴⁴ and $(\text{PDI})\text{CoCl}_2$,¹⁴⁵ which is discussed in Section 2.2.1. In these cases, the high-spin M^{II} ions are bound to neutral PDI^0 ligands. No direct involvement of these species in catalytic transformations have been reported, which can be attributed to the absence of vacant metal orbitals for substrate binding and activation. In contrast, the reduced complexes $(\text{PDI}^{2-})\text{Mn}^{\text{II}}$, $(\text{PDI}^{2-})\text{Fe}^{\text{II}}\text{N}_2$ (**Fe-7a**) and $(\text{PDI}^-)\text{Co}^{\text{II}}\text{Me}$ exhibit singly and doubly reduced **PDI** ligands bound to low spin $\text{Mn}^{\text{II}}/\text{Co}^{\text{II}}$ and intermediate spin Fe^{II} , respectively (Figure 4, left). Importantly, in these electronic configurations, vacant metal orbitals enable the binding and activation of substrates. For example, the iron complex undergoes oxidative addition of biphenylene (Scheme 7). The resulting five-coordinate ferric complex implies that the electron flow is both metal and ligand centered.¹⁴⁶ Such active participation of the **PDI** ligand in oxidative addition^{147–151} and other redox reactions^{141,152–160} was well studied and this $(\text{PDI}^{2-})\text{Fe}^{\text{II}} / (\text{PDI}^-)\text{Fe}^{\text{III}}$ couple is the basis for many catalytic cyclization reactions.¹⁶¹ Similarly, $(\text{Ph}_2\text{PPrPDI})\text{Mn}$ (**Mn-8a**) reacts with trifluoroacetophenone to a ketyl radical complex (Scheme 7).¹³⁶ In this case, electron transfer is a purely ligand centered process. This manganese pincer platform has been utilized in catalytic hydrosilylation of carbonyl compounds.

Scheme 7. Ligand-directed reactions with small molecules.^{136,146,162}

This exemplary reactivity can be attributed to two features (Figure 4, right).^{127,163} High lying, filled orbitals of the reduced pincer ligands serve as reservoir for reducing equivalents allowing the metal complexes to undergo (partially) ligand-based substrate reduction, such as oxidative addition, which is highly unusual for first-row metal ions coordinated by weak-field ligands.^{55,164,165} Furthermore, the Lewis acidity of the metal ions is enhanced by electron transfer to the redox-active pincer ligand and metal low- and intermediate-spin states, thereby offering substrate binding sites. In consequence, strongly reducing metal-pincer platforms result, yet with empty metal-based orbitals for substrate binding

reminiscent of low-spin complexes of low-valent, heavier transition metals stabilized by strong field ligands that are key species in catalysis.^{15,55,70,71,127,166}

Besides the role as electron reservoir, ligand centered radical reactivity that leads to the formation of chemical bonds at the pincer backbone is frequently encountered and is associated with the term chemical-redox non innocence (Scheme 2).^{167–173} In the context of de-/hydrogenation catalysis pincer ligand centered, reversible proton coupled electron transfer seems most relevant combining both concepts of metal-ligand cooperativity and ligand redox activity. While applications in catalysis are much less frequent, an example was given by Goswami and co-workers (Scheme 8).^{174,175} The pyridine-based diazo pincer ligand undergoes stoichiometric, reversible hydrogen atom transfer with the azo/hydrazo couple. This reactivity allowed for application in catalytic aerobic alcohol oxidation. Within the proposed mechanism, the metal serves as template and has no active role with respect to bond formation/cleavage or redox events.

Scheme 8. Azo/hydrazo couple for alcohol dehydrogenation.^{174,175}

The bis(iminopyridyl) ligand (**PDI**), the bis(oxazolinepyridyl) ligand (**Pybox**) and the 2,2':6',2''-terpyridine ligand (**terpy**) are among the most frequently utilized, privileged, potentially redox active pincer ligands. All three ligand classes consist of a central pyridyl unit decorated with imine, pyridyl or oxazoline groups in 2-position, respectively. As a consequence of the rigid character, a meridional 'pincer-type' binding mode is generally favored for all three ligands. The weak-field character predominantly induces high-spin states unless other strong-field ligands are part of the coordination sphere or pincer redox-activity stabilizes lower spin-states. Particularly the **PDI** ligand exhibit distinct redox-active character and can accept up to three electrons,^{176,177} enabling the stabilization of an extended range of redox states and unusual coordination modes.^{144,178,179} The redox properties and coordination chemistry of these ligands with first-row metals will be presented in section 2.2 and applications in de-/hydrogenation catalysis in sections 3-5.

2 PRIVILEGED PINCER PLATFORMS

2.1. Aminopincer Ligands

2.1.1. Diphosphinoamines and Related Ligands

The aliphatic diphosphinoamine ligand family $\text{HN}(\text{CH}_2\text{CH}_2\text{PR}_2)_2$ ($\text{R}^n\text{PN}^{\text{H}}\text{P}$) was extensively utilized in 3d metal catalysis, particularly for de-/hydrogenation reactions. The popularity can be ascribed to some key features:

1) The secondary amine functional group is acidified upon coordination to the Lewis acidic metal. The amide conjugate

base facilitates heterolytic 1,2-addition of H₂ across the M–N bond. The active amide and amine hydride catalyst states are usually generated in situ (Scheme 9). However, the iron amide catalyst (*i*^{Pr}**PNP**)FeH(CO) can be isolated, while the corresponding dihydride amine complex (*i*^{Pr}**P-N^HP**)FeH₂(CO) is only stable under H₂.^{180–182} In comparison, the manganese catalysts (*i*^{Pr}**PN^HP**)MnH(CO)₂ and (*i*^{Pr}**PNP**)Mn(CO)₂ are both isolable.^{183,184} The direct use of these active catalyst species enables catalysis under base free conditions, which can be beneficial to avoid side reactions such as base-catalyzed substrate aldol condensation. In some cases, borohydride precursors, such as (*i*^{Pr}**P-N^HP**)Fe(BH₄)H(CO), can be used as a masked hydride that release BH₃ with weak bases or thermally.¹⁰ Langer and coworkers found catalyst deactivation pathways by borane coordination to the pincer nitrogen donor.¹⁸⁵ Related deactivation products were also found in ammonia-borane dehydrocoupling.^{186,187}

Scheme 9. Generalized proposed outer-sphere hydrogenation mechanism for d⁶ **RPN^HP** pincer catalysts.

Despite the importance of reversible pincer backbone protonation for catalysis, experimentally derived pK_a values of **RPN^HP** amine complexes are surprisingly scarce. Schneider and co-workers reported pK_a values in dms_o-d₆ for the iridium(I) series (*i*^{Pr}**PN^HP**)IrL⁺ (L = PMe₃, cyclooctene, CO; Scheme 10).¹⁸⁸ The results demonstrate the tunability of the N–H pK_a by the ligand environment and the strong acidification with respect to free dialkylamines (pyrrolidine: pK_a^{dms_o} ≈ 44).¹⁸⁹ The pK_a values of the iridium amine complexes are much closer to the dialkylammonium conjugate acids (pyrrolidinium: pK_a^{dms_o} = 11.1).¹⁹⁰ Notably, the MN–H pK_a is in the range reported for some iron dihydrogen and hydride complexes.^{82,191}

Scheme 10. pK_a determination for Ir(*i*^{Pr}**PN^HP**) complexes.¹⁸⁸

2) The strong-field phosphine ligands stabilize active catalyst species in low-spin states avoiding unproductive radical

chemistry. Iron and manganese catalysts generally exhibit d⁶ configuration. In contrast to analogous heavier 4d and 5d catalysts, additional π-accepting strong field ligands are required for first row metals to maintain low-spin configuration, which so far limits the selection of neutral auxiliary ligands for Fe and Mn to CO and isonitriles.¹⁹² For earlier 3d metals, isoelectronic formal V(–I) ((*i*^{Pr}**PNP**)V(NO)₂ / (*i*^{Pr}**P-N^HP**)VH(NO)₂) and Cr(0) ((*i*^{Pr}**PNP**)Cr(NO)(CO) / (*i*^{Pr}**P-N^HP**)CrH(NO)(CO)) analogues of the Fe and Mn platforms were computationally evaluated.^{193,194} Both systems were pointed out as promising candidates for catalytic C=E (E = C, N, O) hydrogenation waiting for experimental confirmation.

3) Within the octahedral geometry, the amine and hydride mutual *cis*-arrangement acts as a template for outer-sphere H⁺/H[–] transfer to the substrate. The strong-field *trans*-ligands, like hydride (Fe) or CO (Mn) increase the hydricity of the transferred hydride and reduce the kinetic barrier of outer-sphere hydrogen transfer to the substrate.^{68,91}

4) The coordinatively and electronically unsaturated five-coordinate amide species that result from H⁺/H[–] transfer are stabilized by the strongly π-donating dialkyl amide ligand. The single-faced π-donor destabilizes a low-lying d-orbital. As a result, the d⁶ (Fe^{II}, Mn^I) complexes preferentially adopt trigonal-bipyramidal geometries with Y-shaped distortion and electronic low-spin configuration.⁵² Importantly, the accessible low-spin state is a prerequisite to subsequent H₂ binding and activation (Scheme 11).

Scheme 11. Generalized proposed inner-sphere hydrogenation mechanism for d⁸ **RPN^HP** pincer catalysts.

The cobalt pre-catalysts with this pincer ligand exhibit distinct structural differences with the Mn and Fe platforms. Hanson's catalyst starts from the square-planar, low-spin cobalt(II) precursor (*i*^{Pr}**PNP**)Co(CH₂SiMe₃) activated *in situ* by Brookhart's acid, which is discussed in Section 3.1.2.¹⁹⁵ Notably, while the iron(II) catalysts show high chemoselectivity for polar multiple bonds,¹⁹⁶ Hanson's catalyst also exhibits high activity for the hydrogenation of unactivated olefins. The different selectivities were attributed to an inner-sphere olefin insertion/σ-metathesis cycle by an *in-situ* formed, square-planar, low-spin cobalt(II) hydride as discussed in Section 3.7.2. In contrast, computational treatment suggests that an MLC-assisted outer-sphere mechanism might be relevant for C=O hydrogenation.^{197,198} Arnold and coworkers also described dinuclear H₂ activation routes for

the CoPNP system.^{199,200} The role of such pathways for catalysis has not been examined. The cobalt catalysts are in general mechanistically less well defined as their iron counterparts. Hanson and coworkers also utilized the aminopincer ligand for nickel(II) catalyzed olefin hydrogenation.²⁰¹

Figure 5. Redox-active PNP ligands.^{202,203}

The Mindiola group reported that the oxidation of nickel(II) diphosphinoanilide complex $[(iPr^rPN^ArP)NiCl]OTf$ (**Ni-9a**) ($E^0 = -0.06$ V vs. Fc/Fc^+) is a mainly ligand centered process (Figure 5).²⁰² Aliphatic analogues of this ligand can be obtained by oxidation of $(tBu^rPNP)M$ complexes ($M = Co, Ni$) with 2,4,6-tri-*tert*-butylphenoxy radical as hydrogen acceptor (Figure 5).^{203,204} As for the diphosphinoanilide nickel(II) complex, oxidation of the aliphatic bromide analogue at -0.19 V is mainly ligand centered. In addition, the aliphatic pincer nickel(II) complex can be protonated at a vinylene bridge ($pK_a^{dmsO} = 0.9$). In consequence, the oxidized complex $NiBr\{N(CHCHPtBu)_2\}^+$ (**Ni-10a**) activates benzylic substrates by C–H hydrogen atom transfer (HAT) with the pincer ligand serving as both electron and proton acceptor.²⁰³ Ligand-centered HAT was also reported by Heyduk and coworkers for a nickel complex with a phenylene-bridged, trianionic SNS pincer (Scheme 12).²⁰⁵ In that case the nitrogen atom serves as proton acceptor. HAT with such radical pincer ligands has not been utilized for catalysis to date.

Schneider and coworkers reported an abnormal CO_2 insertion reaction for the nickel(II) hydride $NiH\{N(CHCHPtBu)_2\}$ (**Ni-10c**) under photolytic conditions (Scheme 13).²⁰⁶ Based on transient spectroscopy, kinetic examinations and trapping experiments the reaction was attributed to a photochemically driven *trans*-NH reductive elimination and subsequent CO_2 activation by nickel(0), representing a photochemical example of metal-ligand-cooperativity. Subsequently, photo-driven reverse water-gas-shift could be established within a two-step synthetic cycle (Scheme 13).²⁰⁷ H_2 heterolysis proceeds by proton transfer to a pincer backbone vinylene bridge emphasizing the relation as aliphatic analogues of the pyridine based PNP pincer ligands, which is discussed in Section 2.2.1.

Scheme 12. Thermochemical Cycles for the BDFE determination of C–H HAT (**Ni-10b**) and N–H HAT (**Ni-11a**) reactivity.^{203,205}

Scheme 13. Reactivity of Dehydrogenated Amido Pincer Ni(II) Complexes Towards CO_2 and Two-Step Photochemically Driven Reverse Water-Gas Shift Chemical Cycle ($P = PtBu_2$).²⁰⁶

2.1.2. BPI and Boxmi Ligands Gade and co-workers reported a series of indolene based NNN-pincer ligands with different backbones (Figure 6). The spin density distribution in the four-coordinate, divalent iron complex with a 1,3-bis(2-pyridylimino)isoindolines ligand was examined by

means of ^{13}C NMR spectroscopy.²⁰⁸ Iron, cobalt and manganese complexes with this family of ligands were utilized in enantioselective ketone reduction,²⁰⁹ enantioselective ketone hydrosilylation,^{210,211} and enantioselective ketone hydroboration.^{212,213}

Figure 6. Boxmi and PdmBox ligands.^{214,215}

2.1.3. Aminophenol Pincer Ligands Bulky phenols can form stable phenoxo radicals.²¹⁶ Accordingly, phenolic substituents were used as building blocks in redox-active pincer ligands.²¹⁷ The amino phenol NNO^{ISQ} ligand used in $(\text{NNO}^{\text{ISQ}})\text{FeCl}_2$ (**Fe-12**) was initially utilized for palladium mediated, intramolecular C-H amination.²¹⁸ The Fe complex exhibits high-spin iron(III) antiferromagnetically coupled to a pincer radical anion. CV measurements showed one quasi-reversible reductive wave at -0.74 V (vs. Fc/Fc^+) and one quasireversible oxidation at 0.51 V (vs. Fc/Fc^+), which are both proposed to be ligand centered. This compound catalyzes intramolecular $\text{C}(\text{sp}^3)\text{-H}$ amination.²¹⁹ The NNO^{ISQ} ligand is also available with a tethered phosphine group, which was utilized for ligand centered disulfide activation.²²⁰

Figure 7. Redox-active aminophenol ligands.^{219,221}

The cobalt complex $(^{\text{d}}\text{OCO})\text{Co}(\text{thf})$ (**Co-13**) (Figure 7) was reported by Soper and co-workers as a low spin Co(II) species with a dianionic, closed-shell bisphenolate ligand.²²¹ Three redox states were detected by CV as quasi reversible events at -0.32, 0.30 and 0.77 V, respectively, and proposed to be not exclusively metal centered. Chemical oxidation gave rise to the mono and dicationic species best described as cobalt(II) in both cases.²²¹ Related amino-diamine ligands are redox-active but have a facial coordination motif and are thus no further discussed in this review.²²²

2.1.4. Dihydrazonepyrroles Anderson and co-workers recently reported the design of a novel dihydrazonepyrrol ligand (Figure 8).²²³ The ligand architecture represents a modification of known diiminopyrrole ligands to

avoid undesired bidentate coordination modes upon introduction of sterically shielding substituents and an extended backbone.

Figure 8. Dihydrazonepyrrol ligand and coordination with nickel.²²³

Coordination of nickel gave a square planar trimethylphosphine complex. EPR-Spectroscopy confirmed a ligand-centered radical and computational analysis revealed the majority of the spin density on the ligand giving rise to formulation as divalent nickel in complex **Ni-14**. This complex is prone to oxidation and reduction both as ligand-centered processes. Furthermore, reversible hydrogen atom transfer was observed.²²³

2.2. Pyridyl Pincer Ligands

2.2.1. Diphosphinopyridine and Related Ligands The diphosphinopyridine ligands $\text{NC}_5\text{H}_5\text{-2,6-(CH}_2\text{PR}_2)_2$ ($\text{R}^n\text{PN}^n\text{P}$) represent an archetypal cooperative ligand class. Fe(II), Co(II) and Ni(II) metal complexes with PN^nP ligands were first reported in 1971 by Nelson and coworkers.²²⁴ The cyclic backbone results in more rigidity compared to the PN^nP ligand, but the pincer ligand arms still allow for some degree of conformational freedom. Milstein introduced a concept to catalysis that is referred to as “aromatization-dearomatization” as a distinctive feature of the $\text{R}^n\text{PN}^n\text{P}$ platform.^{108,109,225} Several analogies and differences with respect to the aliphatic PNP are apparent:

1) The benzylic methyl protons of 2-methylpyridine exhibit a pK_a in THF around 35.²²⁶ Accordingly, the free pincer ligand can be deprotonated once and even twice by strong bases like KCH_2Ph ($\text{pK}_a^{\text{THF}} \approx 42$) and $\text{LiCH}_2\text{SiMe}_3$, respectively, giving the corresponding alkali salts enabling the synthesis of “dearomatized” transition metal complexes via salt metathesis.^{227,228} However, more common access, e.g. to Re,²²⁹ Ru,^{230–232} Rh,²³³ Ir,^{234,235} Ni,²³⁶ Pd^{237,238} and Pt^{237–239} complexes, is provided by dehydrohalogenation after coordination of the neutral diphosphinopyridine ligand to transition metal ions. Benzylic deprotonation is stabilized by charge delocalization within the pyridyl core. The relevance of the amido resonance structure is evidenced by a shortened C-C bond in the pincer backbone, in analogy to the aliphatic enamido pincer ligand.²⁰⁴ Milstein and coworkers also demonstrated the two-fold benzylic deprotonation of a nickel(II) complex with methyllithium.²³⁶ Recently, the Ozerov group could isolate a dearomatized rhenium diphosphinophenyl complex.²⁴⁰

2) The PNP ligands in combination with additional strong field ligands (hydride, CO) stabilize d^6 low-spin states of 3d

metals, which enables binding of substrates like H₂. In comparison with the dialkylamido pincers, the weaker π -donation by the dearomatized ligands further increases metal Lewis acidity. For example, in contrast to (*t*BuPN^{II}P)Fe(H)₂(CO) (see above), the *trans*-dihydride complex (*t*BuPN^{II}P)Fe(H)₂(CO) could be isolated.²⁴¹ In turn, the dearomatized monohydride complex could only be isolated with an additional sixth ligand.¹⁰⁷ Alternative access to octahedral, aromatized hydride catalyst species is provided by thermal activation of borohydride complexes, which allows for base-free catalysis.

3) The ligand-centered basicity of dearomatized PN^{II}P complexes enables the heterolysis of substrates like H₂ with (re)aromatization of the pyridyl moiety and formation of a M–H bond (Scheme 14).¹⁰⁷ The 1,3-addition is a distinguishing feature with respect to the aliphatic amidopincer systems (1,2-addition).

Scheme 14. General Cooperativity Mechanism of the PN^{II}P Pincer Complexes with d⁶ Electronic Configuration for Activation and Addition of Dihydrogen Across Different C–C-, C–N- and C–O-Multiple Bonds.

Regarding first row metals, particularly iron(II) and to a lesser extent manganese(I) complexes have been utilized for hydroelementation catalysis due to facile accessibility of d⁶ low-spin precatalysts. Metal-ligand cooperative reactivity for isoelectronic cobalt(III) complexes is not known to date. Milstein and coworkers reported the formal loss of a hydrogen atom at the CH₂ linker of a d⁸ pyridyl pincer Co(I) methyl complex.²⁴² Unlike the corresponding PDI complex (see below), the methyl complex (*t*BuPN^{II}P)CoMe (**Co-1a**, Figure 9) features low-spin cobalt(I) as a consequence of the higher lying pincer acceptor levels. This compound undergoes hydrogen atom loss at one of the methylene bridges, and the resulting product was initially described as low-spin cobalt(I) bound to a radical pincer ligand.²⁴² This assignment was later revised for cobalt(II) with a dearomatized, anionic pincer ligand (**Co-1b**) based on EPR characterization and supporting DFT studies.^{243,244}

Figure 9. Comparison in the electronic structure between cobalt methyl PNP complexes.^{242,243}

Van der Vlugt and coworkers reported the synthesis of dearomatized nickel(II) complexes and 1,3-addition of benzenethiol.²⁴⁵ The same group also explored the coordination chemistry and reactivity of copper(I) complexes with dearomatized ligands,^{246,247} providing evidence for metal-ligand cooperativity in copper catalyzed [2+3] cycloaddition of phenylacetylene and benzyl azide.²⁴⁸ Early transition metals complexes (Sc, Ti, V) with this ligand have not been reported and chromium complexes are rare.²⁴⁹

Figure 10. PN₃P and PN₅P ligands.

In analogy to the parent PN^{II}P ligand, the pyridine aminophosphine ligands **PN₃P** and the pyrimidine-based **PN₅P** pincer ligand was extensively used in catalysis (Figure 10). Manganese, iron and cobalt catalysts with **PN₃P** and **PN₅P** ligands were established by the groups of Kirchner and Kempe, respectively.^{113,250} The exocyclic NH-bridges of both **PN₃P** and **PN₅P** ligands are more acidic than the benzylic groups of the parent PN^{II}P ligand, giving rise to substrate activation by 1,3-addition at dearomatized ligands. Heterolytic cleavage of dihydrogen was reported with an Fe(**PN₃P**)-complex after reduction of one of the NH-moieties with zinc powder.²⁵¹

Nickel(II) **PN₃P** and **PN₅P** pincer complexes were utilized as catalysts for Suzuki-Miyaura,²⁵² Kumada-Corriu and Negishi cross-coupling reactions.²⁵³ Copper(II) **PN₃P** catalysts were utilized for Suzuki-Miyaura cross-coupling.²⁵⁴ Early transition metal complexes (Sc, Ti) were not reported. Vanadium and chromium complexes are scarce and chromium complexes were used as catalysts in olefin oligomerization.^{255–257}

2.2.2. Pyridinediimines and Related Ligands

The pyridinediimine (PDI) pincer family represents one of first privileged ligands that sparked the current developments in 3d metal catalysis. After Brookhardt's and Gibson's landmark discoveries of the remarkable catalytic activity of iron and cobalt **PDI** complexes in ethylene polymerization,^{258–260} numerous studies have been conducted^{258,261–281} and were thoroughly reviewed.^{282–286} The synthetic modularity and accessibility offer modifications that give rise to many applications of **PDI** ligands in 3d-metal catalyzed C–

C coupling^{158,161,165–167,287–294} de-/hydrogenation,^{295–299} hydrosilylation,^{295,298,300,301} hydroboration,³⁰² and electrochemical transformations.³⁰³ Its use in iron catalysis was inspired by isolobal relationship considerations of the Fe(CO)₃-fragment with (PDI)Fe.^{305–308} Low-lying PDI π^* -orbitals support electron-rich, active key species in catalysis.

Three key positions within the PDI platform have been systematically varied with significant effects on the redox properties and chemical reactivity, i.e. (a) the 4-position of the pyridine core, (b) the substitution pattern of the C_{imine}-atom, and (c) imine *N*-substitution (Figure 11). Free PDI ligands generally exhibit electrochemically reversible PDI/PDI^{•−} redox couples below −2.5 V (vs. Fc/Fc⁺), such as the ‘archetypical’ ⁱPrPDI ligand ($E^0 = -2.62$ V).

Figure 11. PDI ligands and their redox potentials.^{308,309}

Substitution in the pyridine *para*-position has a strong effect on the ligand acceptor orbitals and allows for precise fine tuning the reduction potential by almost $\Delta E^0 = 0.5$ V.^{308,309} Phenyl vs. methyl substitution at the C_{imine} position shifts the reduction potential anodically, yet less significantly, by about 0.1 V,³⁰⁹ enabling, e.g. the stabilization of an electron rich iron(I) dinitrogen complexes with a trianionic PDI ligand. However, phenyl substitution in this position can lead to irreversible catalyst deactivation pathways.^{152,158,295}

The reduced radical ligand Na(ⁱPrBPDI) was characterized by X-band EPR spectroscopy at room temperature.³⁷⁴ A sharp, isotropic 10 line signal at $g_{iso} = 2.003$ was observed. Simulations revealed hyperfine interactions (HFI) with the pyridine ($A_{iso} = 6.2$ MHz) and imine ($A_{iso} = 3.3$ MHz) ¹⁴N nuclei, the *para*-hydrogen atom ($A_{iso} = 14.0$ MHz) and the ²³Na counter cation ($A_{iso} = 8.4$ MHz). The EPR spectrum of the ⁱPrPDI radical anion is more complex presumably due to additional HFI with the imine methyl groups.

Figure 12. Influence of the second coordination sphere on the redox potential.^{310–312}

Exchange of the *N*-aryl vs. a more electron rich, aliphatic cyclohexyl substituent moves the reduction potential cathodically by about 100–200 mV (Figure 11).³⁰⁹ Variation of the *N*-aryl *ortho*-substituents has a much weaker impact on reduction potentials, but can strongly alter rates and equilibria of transition metal complex reactivity.^{152,295,309,313} For example, the common iron N₂ precatalyst platform forms *ortho*-bridged dinuclear species with sterically less demanding *ortho*-aryl substituents at the *N*-phenyl rings.³¹³ Amino or boryl substitution in *ortho*-position, had a rather insignificant effect (<40 mV) on the reduction potential of transition metal complexes (Figure 12).^{310,311} Redox fine-tuning was reported by introducing crown ether fragments as N_{imine}-substituents.^{312,314} Ion coordination, to the crown ether moiety resulted in an anodic shift of about 50 mV (Figure 12).^{312,314}

Figure 13. Electronic structure of the four- and five-coordinate iron PDI dinitrogen complexes.^{137,153,298}

The distinct redox activity of the PDI ligand platform necessitates the use of spectroscopic and computational methods for unambiguous oxidation state assignments. For example, Chirik’s five-coordinate bisdinitrogen complex (PDI)Fe(N₂)₂ (Fe-7j) exhibits a closed-shell electronic structure, as expressed within ferrous ($[(PDI)^2Fe^{II}(N_2)_2]$) or zerovalent iron ($[(PDI)^0Fe^0(N_2)_2]$) resonance structures (Figure 13).¹³⁷ In contrast, the four-coordinate mono-N₂ complex (Fe-7a) (best described as Fe(II) with intermediate spin configuration antiferromagnetically coupled to a triplet PDI diradical ligand).¹³⁷ Replacement of the labile dinitrogen ligands by stronger field ligands gives rise to both four and five-coordinate iron(0) complexes.^{178,315} In comparison with the ketimide platform, the iron aldimide system was found to be less electron rich and did not form N₂ complexes.³¹⁶

Figure 14. Electronic structure of the cobalt complexes **(PDI)CoN₂** (**Co-7a**) and **(PDI)CoMe** (**Co-7b**).^{154,317}

Reduction of the cobalt(II) high-spin complex **(PDI)CoCl₂** is ligand centered giving the square-planar *d⁷* low-spin complex **(PDI^{•−})Co^{II}Cl**.³¹⁷ Antiferromagnetic coupling result in an overall *S* = 0 ground states for the chloro and respective alkyl complexes.^{154,317} In analogy, the dinitrogen complex **(PDI^{•−})Co^IN₂** (**Co-7a**) that results from reduction of the chloride under dinitrogen was described as low-spin cobalt(I) with a monoanionic PDI radical ligand. **(PDI)CoN₂** (**Co-7a**) is prone to both ligand centered oxidation and reduction, emphasizing the intriguing redox behavior of the PDI ligand.^{154,167,258,317,318} Direct comparison with the analogous iron(II) complex showcases the higher ionization potential of cobalt, which results in a lower oxidation state and less reduced PDI ligand.

In comparison, manganese PDI complexes are less well explored.³¹⁹ **(PDI)MnX₂** (X = halide) and **(PDI)Mn(thf)₂** both feature high-spin manganese(II), i.e. in the latter case antiferromagnetically coupled to a dianionic PDI^{2−} diradical ligand, giving an overall *S* = 3/2 ground state.¹⁵⁹ These compounds proved inactive as precatalysts in ethylene polymerization,³²⁰ and most reactions that are catalyzed by iron and cobalt PDI complexes, such as olefin hydrogenation or diene cycloisomerization. In contrast to iron and cobalt, low-valent **(PDI)M(N₂)_n**-type reduction precatalysts with labile dinitrogen ligands could not be obtained, presumably due to weak backbonding from high-spin Mn(II) to N₂. These findings emphasize the accessibility of non-high-spin, low-valent metal states as a prerequisite for redox transformations, such as oxidative addition.

Figure 15. Electronic structures of the five coordinate manganese complexes **(PPh₂PrPDI)Mn** (**Mn-8a**) and **(PPh₂EtPDI)Mn** (**Mn-8c**).^{34,301,321}

Trovitch and coworkers reported important contributions for manganese catalyzed hydroelementation by introduction of modified PDI ligands with two additional diphenylphosphine groups tethered to the imine nitrogen atom (Figure 15).³⁴ Two alternative descriptions for the electronic structure of **(PPh₂PrPDI)Mn** (**Mn-8a**) were given. Based on

EPR studies the overall doublet ground state was initially attributed to low-spin manganese(II) bound to a dianionic, closed-shell PDI^{2−} ligand.³⁰¹ Subsequent DFT studies gave a possible alternative description as intermediate-spin manganese(II) strongly antiferromagnetically coupled (*J* = −401 cm^{−1}) to a triplet PDI^{2•−} diradical ligand.¹³⁶ Shortening of the propylene linker leads to the dinuclear complex **{(PPh₂EtPDI)Mn}₂** (**Mn-8c**) (Figure 15) with bridging imine groups as the ethylene bridges prevent coordination of both phosphine side chains.¹⁷⁵ The overall triplet ground state was rationalized with two intermediate-spin manganese(I) ions that are antiferromagnetically coupled to singly reduced PDI^{•−} radical anions. In solution, dissociation of the dimer is proposed.

The general preference for non-high-spin states with this modified PDI platform can be attributed to the additional strong field phosphine donors and gives rise to application in catalysis.^{34,321,322} **(PPh₂PrPDI)Mn** (**Mn-8a**) catalyzes the hydrosilylation of ketones. The hydride complex **(PPh₂PrPDI)MnH** (**Mn-8d**) was isolated and its role in catalysis investigated. The geometric data suggest a doubly reduced closed-shell PDI^{2−} ligand and low-spin Mn^{III}, as a consequence of the strong field hydride ligand. In fact, stabilization of the PDI^{2−} singlet state was also attributed to the strong hydride *trans*-influence, leading to destabilization of one PDI π* acceptor orbital, which favors spin-pairing.¹³⁶

Figure 16. Electronic structures of manganese complexes **(PPh₂PrPDI)MnH** and **(PyEtPDEA)Mn**.^{34,136,323}

The phosphine side chains were also replaced by ethylene pyridine arms.³²³ Reduction of a dihalide precursor with excess Na/Hg gave a five-coordinate bisenamide species (Figure 16). Deprotonation of the methyl groups truncates the PDI π-system thereby raising the π* acceptor levels. This ligand is therefore not redox-active. This complex is best described as intermediate-spin Mn^{II} with a closed-shell bisenamido PDI ligand. Notably, other deprotonated PDI manganese complexes were shown to undergo dimerization by C-C bond formation.³²⁴

Nickel PDI complexes are comparatively scarcely examined. Wieghardt and co-workers examined a series of octahedral complexes **(PDI)₂M(PF₆)_n** (M = Mn, Fe, Co, Ni, Cu, Zn).³²⁵ A four-coordinate nickel PDI complex was first reported by Manuel and Rohde.³²⁶ The distorted square-planar complex **(PDI)NiCl** (**Ni-7a**) was described as nickel(II) and a PDI^{•−} radical ligand. Reduction with NaH under N₂ leads to the square-planar complex **(PDI)^{2−}Ni^I(N₂)** (**Ni-7b**) with a closed shell dianionic ligand.¹⁶⁷

In contrast, the bisaldimine PDI complexes (**PDI**)NiX (X = Cl, Br) are best described as nickel(I) species.³²⁷ The d^9 configuration is associated with distortion from square-planar geometry. Unlike Rohde's system this complex does not undergo ligand centered oxygenation reaction by air as a consequence of the metal centered radical character.

Figure 17. Electronic structures of complex different nickel PDI and NDI complexes.^{167,326,328}

Uyeda and coworkers expanded this ligand platform to the to naphthyridinediimine (NDI; Figure 17), which offers two adjacent bonding sites for the stabilization of bimetallic complexes. Furthermore, the extended π -system enables improved electron storage. (**NDI**)Ni₂(C₆H₆) (**Ni-16**) (Figure 17) was described as a dinickel(I) complex with the two metal ions in a bonding distance ($D_{Ni-Ni} = 2.496(1)$ Å) bound to a dianionic NDI²⁻ ligand. Remarkably, this compound exhibits four (2 metal- and 2 ligand-centered) reversible reductions between 0 and -3.0 V (vs. Fc/Fc⁺), pointing out the ability of this platform to undergo multi-electron redox processes within accessible potentials.³²⁸

The analogous iron and cobalt complexes, [(**NDI**)M₂(C₆H₆)] (M = Fe, Co), were subsequently reported.³²⁹ In contrast to the nickel and the cobalt complexes ($S = 0$ ground state) the iron complex exhibits four unpaired electrons ($S = 2$ ground state).

2.2.3. Terpyridine The scope of applications for the **terpy** ligand is more diverse than for **PDI** and **Pybox** ligands, including many photochemical applications,^{43,330–336} but also as building block in supramolecular chemistry,^{337–340} magnetochemistry,³⁴¹ and catalysis.^{1,4,73} Moreover, the role of terpy redox activity in nickel catalyzed C-C bond formation was recently discussed.^{342–346}

PDI and terpy ligands show similar redox properties. Although the terpy ligand class (tpy = 2,2':6',2''-terpyridine) is widely established and utilized for decades, redox non-innocent ligand behavior was evaluated more recently.³⁴⁷ The free terpy ligand exhibits a reversible reduction at -2.55 V (vs. Fc/Fc⁺) and an irreversible reduction event at around -3.06 V (Figure 18).^{348,349} As an example of ligand non-innocence, the four reduction events of the chromium complex [Cr^{III}(tpy)₂] are all ligand centered as shown by K-edge X-ray absorption spectroscopy and DFT calculations.³⁵⁰ In contrast, the homoleptic cobalt complexes [Co(tpy)₂]ⁿ⁺ prefer metal based redox steps.³⁵¹ Palladium and platinum complexes of the related 2,5-bis(α -pyridyl)pyrrolate ligand also showed ligand based redox events which are cathodically shifted due to the anionic ligand character.³⁵² Redox non-innocence was reported to stabilize unusual oxidation states,

like an square pyramidal Ni(III) species.³⁵³ Analogous triazol-based ligands were also reported.^{354,355}

Figure 18. terpy ligand and its redox potential.³⁴⁹

The close energetic proximity of the terpy acceptor orbitals with respect to nickel d-levels is showcased by EPR spectroscopic examination of the complexes (tpy)NiX (X = Me, Br). The strong-field methyl ligand results in terpy reduction, (tpy⁻)Ni^{II}Me (**Ni-9**), while (tpy)Ni^IBr (**Ni-10**) is best described as a nickel(I) complex with neutral terpy.^{356,357} Both nickel complexes show similar electrochemical behavior.

Figure 19. Electronic structure of the nickel terpy complexes (tpy)NiMe (**Ni-17a**)³⁵⁶ and (tpy)NiBr (**Ni-17b**)³⁵⁸ and the corresponding redox potentials (potentials were re-referenced to the Fc/Fc⁺ couple according to ref 359).

Chirik and coworkers reported the divalent iron complex (tpy)Fe(CH₂SiMe₃)₂ (**Fe-17**) as a precatalyst for olefin hydrosilylation (Figure 20).³⁶⁰ Magnetochemical, spectroscopic and computational evaluation support the description as a high-spin ferric complex with an antiferromagnetically coupled, anionic terpy radical ligand resulting in an overall $S = 2$ ground-state. On the contrary, the related complex (tpy)Co(CH₂SiMe₃) (**Co-17**), which is a hydroboration catalyst, exhibits an $S = 0$ ground-state as a result of low-spin cobalt(II) coupled to the terpy⁻ radical ligand (Figure 20).³⁶¹

Figure 20. Terpy complexes of iron and cobalt and their electronic structure.^{360,361}

2.2.4 Pybox Bis(pyridyl)oxazoline (**Pybox**) complexes were extensively utilized in asymmetric catalysis, as this ligand allows for the synthetic introduction of chiral moieties at the oxazoline framework with strong stereochemical induction.^{362–367} In contrast, the electronic structures of Pybox bearing (pre)catalysts are less well explored. Comparison of Pybox and PDI as free ligands and within coordination compounds was initially carried out by Chirik and coworkers.³⁰⁹ Reduction potentials of several free PDI and Pybox ligands were found within 20 mV. However, comparison of the CO stretching vibrations of the complexes $[(L)Fe(CO)_2]$ ($L = iPr$ -**Pybox**, **PDI**) showed lower values for the Pybox complexes by about 40 cm^{-1} , pointing out stronger donation by this pincer ligand. Importantly, (**Pybox**) $FeCl_2$ does not react with dinitrogen under reductive conditions but forms the bis-chelate species (**Pybox**) $_2Fe$. This reaction was pointed out as a catalyst deactivation pathway in ketone hydrosilylation.³⁰⁹

Figure 21. Pybox and the corresponding redox behavior.³⁰⁹

The similarities between PDI, terpy, and Pybox ligands was further illustrated by ^{57}Fe Mössbauer spectroscopic examination of a series of five-coordinate dialkyl iron complexes.^{309,360} (iPr -**Pybox**) $Fe(CH_2SiMe_3)_2$, (**terpy**) $Fe(CH_2SiMe_3)_2$, and (Et -**PDI**) $Fe(CH_2SiMe_3)_2$ all feature high-spin iron(III), antiferromagnetically coupled to pincer ligand radical anions. Schley and Fu conducted a mechanistic study on Ni (**Pybox**)-catalyzed, stereoselective Negishi cross-coupling, and defined (**Pybox**) $NiPh$ as Ni^{II} with a pincer radical anion.³⁶⁸ In general, the relevance of redox non-innocence for catalysis is less well explored for Pybox.

2.2.5. Pyridyldicarbenes Most reported CNC pincer complexes feature 4d and 5d metals.³⁶⁹ Cobalt and iron complexes with the strongly donating pyridyldicarbene pincer ligands first reported by Danopoulos,^{370–372} and evaluated in catalysis in a comparative study by Chirik and co-workers.^{289,373,374}

Figure 22. Iron and Cobalt pyridyldicarbene (CNC) pincer complexes.^{289,373,374}

The N_2 -stretching vibrations of five-coordinate iron dinitrogen complexes are shifted to smaller wavenumbers by about

20 cm^{-1} for the CNC series.^{298,370} The free CNC-pincer showed no accessible electrochemical reduction but could be reduced chemically, as determined by EPR-spectroscopy.³⁷⁴ Unlike for (**PDI**) $Fe(N_2)_2$, dissociation of a dinitrogen ligand was not found in solution. Detailed spectroscopic and computational analysis are in agreement with iron(0) and a neutral dicarbene pincer ligand.²⁸⁹ The cobalt methyl complex (Figure 22) is a low spin Co^{II} species with an antiferromagnetically coupled radical ligand.³⁷⁴ The radical ligand undergoes side reactions like alkyl migration onto the ligand backbone.³⁷⁵

2.2.6. Iminopyridine and Related Systems

Bidentate iminopyridine (**IP**) ligands, which exhibit a truncated π -system with respect to PDI, can also be redox non-innocent. This is illustrated by a series of tetrahedral 3d metal complex (**IP**) $_2M$.³⁷⁶ Huang and coworkers developed an iminopyridine-based pincer ligand extended by one additional phosphinite arm (Figure 23).³⁷⁷ The free ligand can be reversibly reduced at -2.74 V (vs. Fc/Fc^+), i.e. a mild cathodic shift of 120 mV with respect to PDI, assigning to the phosphine moiety, which is a general stronger donating group in contrast to imine group in the PDI ligand. In a series of iron carbonyl complexes the C-O stretching vibration of a PNN complex was bathochromically shifted by approximately 100 cm^{-1} with respect to the corresponding PDI complex.³⁷⁸

Figure 23. Oxazoline iminopyridine and phosphinite iminopyridine and their redox potential.³⁷⁷

Complexation with ferrous chloride gives the five coordinate d^6 high-spin species ($tBuPNNiPr$) $FeCl_2$. The reduced dicarbonyl complex ($tBuPNNiPr$) $Fe(CO)_2$ exhibits a reversible reduction at -2.54 V, i.e. slightly lower than the PDI congener.³⁰⁸ In analogy to the PDI system, DFT computations support iron(I) with a singly reduced pincer ligand.³⁷⁷ However, low-valent dinitrogen complexes were not reported and catalytic experiments were only performed by *in situ* reduction. Due to the potential lability of the phosphinite group with respect to P-O cleavage the oxygen linker was also replaced by a methylene group.³⁷⁹ Alternatively, Huang and coworkers reported the synthesis of a bipy-based PNN-pincer with a phosphine side arm. The redox properties of these ligands have not been investigated in detail.³⁸⁰

The same group developed an NNN-pincer ligand that combines the PDI and the chiral Pybox frameworks (Figure 23).³⁸¹ This ligand has been applied to manganese-, iron- and cobalt-catalyzed asymmetric hydrogenation, hydroboration and hydrosilylation.^{382–386} Electronic structure investigations of catalytically relevant model complexes were not reported.

2.2.7. Bipyridine Based Pincer Ligands Redox-active 2,2'-bipyridine^{347,387–389} ligand has been introduced as a building block for PNN and NNN pincer ligands. The phosphine tethered bipyridine ligand **PhBPP** (Figure 24) was utilized in copper catalyzed CO₂ electroreduction.³⁹⁰ Facile dearomatization of an iron complex was reported by Milstein and co-workers.³⁹¹ The electronic properties of **R,R'****BPI** with respect of ligand centered redox-activity are yet to be explored.³⁹²

Figure 24. Bipyridine based pincer complexes.^{390,392}

2.2.8. Azaphenyl Ligands and Related Systems

The scope of tridentate NNN-type ligands was extended by Goswami upon attaching phenylazo groups to a central pyridine core (Figure 25).^{393–395} In analogy to the PDI platform, a low lying, energetically accessible π^* orbital is located at the azo unit. The free PDAz ligand exhibits two reversible reductions at -1.79 V and -1.47 V (vs. Fc/Fc⁺), respectively, i.e. is a large anodic shift of around 750 mV with respect to the PDI platform. The one-electron-reduced radical ligand could be isolated from bulk electrolysis.³⁹⁶

Figure 25. Electronic properties and redox potentials of **PDAz**³⁹⁶ and corresponding nickel(II)¹⁷⁵ and zinc(II)¹⁷⁴ complexes.

An octahedral, high-spin nickel(II) complex with this ligand (**Ni-19a**, Figure 25) was used as an alcohol dehydrogenation catalyst, which is discussed in Section 4.1.2.¹⁷⁵ Four reversible and quasi-reversible reductions were found in a range between -0.44 V and -1.69 V and assigned to stepwise population of the ligand π^* orbitals. Two reversible reductions at -1.17 and -0.59 V were obtained for the corresponding zinc complex (**Zn-19**).¹⁷⁴

The combination of phenylazo and phenanthroline building blocks gave rise to the PhenAz ligand (Figure 26). This NNN-pincer ligand exhibits a reversible reduction at -1.39 V suggesting potential redox non-innocence. Introduction of a *para*-chloro substituent at the phenyl moiety only slightly shifts the reduction potential ($\Delta E^\circ = 0.02$ V). Unlike the symmetric PDAz ligand, this ligand shows one reversible and one irreversible reduction.³⁹⁷

Figure 26. Redox potentials of ligand **PhenAz**³⁹⁷ and a ferric iron complex (potentials were re-referenced to the Fc/Fc⁺ couple according to ref 359).³⁹⁷

Complexation with ferrous chloride leads to a five-coordinate dichloride that was described as iron(II) high-spin coordinated to a neutral pincer ligand. This compound exhibits a reversible reduction at -0.71 V and irreversible reduction at -1.23 V (vs. Fc/Fc⁺). Both the free ligand and the iron complex (**Fe-20**) undergo reduction in the presence of KOtBu. In both cases, isotropic EPR spectra with similar g-values ($g = 1.997, 2.004$) were obtained suggesting ligand centered reduction in the latter case. The possible relevance for catalytic dehydrogenation of secondary alcohols is discussed below.³⁹⁷

2.2.9. Bis(pyrazolyl)pyridine

The Bis(pyrazolyl)pyridine (**PDPz**) was first characterized electrochemically by Caulton and co-workers.³⁹⁸ Within a potential window of more than 4 V no reversible redox events were observed reflecting the electron rich character in comparison to the PDI ligand. This is confirmed by the CO stretching vibration of corresponding zerovalent iron complexes. Accordingly, redox activity of the pincer was not observed. However, the deprotonated ligand (for R' = H) can serve as a proton relay in metal-ligand cooperative H–X heterolysis³⁹⁹ and was N-borylated by HBpin in case of a related PNN pincer.⁴⁰⁰ The related bis(pyrazolide) pincer ligand exhibits no reductive features and three irreversible oxidative redox events in the CV.⁴⁰¹

Figure 27. Bis(pyrazolyl)pyridine as pincer ligand.⁴⁰²

2.2.10. Phosphaalkene Pincer Ligands

The phosphaalkene pincer ligand BPEP is less explored and has significantly different properties than the isoelectronic PDI due to very low lying π^* -orbital.⁴⁰³ Electrochemical characterization of a benzodiphosphaalkene pincer revealed reversible reduction.⁴⁰⁴ Ozawa and Nakajima reported the synthesis of the iron complex (**BPEP**)FeBr, which features high-spin iron(I) with a strongly distorted trigonal monopyramidal structure.⁴⁰⁵ This contrasts with the corresponding

square-planar iron(II) PDI complex. To date, only a handful reactivity studies have been exemplified,^{406–408} catalytic studies have not been carried out yet.

Figure 28. Bis(phosphaethenyl)ligands.⁴⁰⁵

3 HYDROGENATION

3.1. Hydrogenation of Ketones and Aldehydes

3.1.1. Pyridyl-Based and Related Pincer Catalysts

The first iron pincer catalyst for ketone hydrogenation was reported in 2011 by Langer et al. (Scheme 15).¹⁰⁷ The precatalyst $[(i^{\text{Pr}}\text{PN}^{\text{Py}}\text{P})\text{Fe}(\text{H})\text{Br}(\text{CO})]$ (**Fe-1c**) catalyzes the reduction of several ketones in ethanol with low catalyst loading at mild conditions (4.1 atm H_2 , r.t.) upon activation with base (KOtBu). High turnover numbers (1880 @ r.t.; 1720 @ 40 °C) and frequencies (430 h^{-1} @ 40 °C) were achieved for the benchmark substrate acetophenone. While electronic effects by the arylketone *para*-substituents (-Me, -Cl) were small, potentially donating groups (-CN, - NH_2), strongly inhibit catalysis. α,β -Unsaturated ketones exhibit low chemoselectivity and aliphatic ketones like cyclohexanone give medium yields under these conditions.

Scheme 15. Iron-catalyzed ketone hydrogenation reported by Langer et al.¹⁰⁷ a: 0.1 mol% catalyst and 0.2 mol% KOtBu.

Langer et al. later expanded this catalyst platform by the borohydride analogue $[(i^{\text{Pr}}\text{PN}^{\text{Py}}\text{P})\text{Fe}(\text{H})(\text{CO})(\eta^1\text{-HBH}_3)]$ (**Fe-1d**) which enables catalysis under base-free conditions. However, low catalytic activity is obtained at room temperature due to the necessity of thermal borane dissociation for catalyst activation.⁴⁰⁹ Similar catalytic activities are obtained for **Fe-1c** at r.t. and **Fe-1d** at 40 °C, respectively (0.05 mol%; $\text{TOF}_{\text{Fe-1c}} = 430 \text{ h}^{-1}$, $\text{TOF}_{\text{Fe-1d}} = 296 \text{ h}^{-1}$). The substrate scope is similar, yet with remarkable catalytic activity for 2-acetylpyridine in case of **Fe-1d**.

Fe-10a/Fe-11 are also active catalysts for aldehyde hydrogenation (Table 1).^{107,409} Considerably lower turn-over

numbers were initially obtained under the same conditions ($\text{TON}_{\text{PhC(O)H}} = \text{ca. } 300$). The authors attributed the reduced yield to catalyst inhibition upon formation of benzoic acid via a base-catalyzed Cannizzaro reaction. This rationale lead to strongly improved catalytic performance by addition of base to prevent catalyst inhibition by acidolysis.⁴¹⁰ Accordingly, in the presence of excess NEt_3 (30 atm H_2) the TON for benzaldehyde hydrogenation could be improved by more than an order of magnitude (Table 1). This protocol gives excellent yields for the hydrogenation of secondary and tertiary aliphatic as well as aromatic aldehydes with low catalyst loadings (0.025 mol%). Primary aliphatic aldehydes are not suitable substrates due to competing aldol condensation. Low yields for 4-bromo- and 4-chlorobenzaldehyde are attributed to oxidative substrate esterification with the solvent to give the respective ethylbenzoates.

Stoichiometric control experiments were conducted to examine the reaction mechanism.¹⁰⁷ Deprotonation of the pincer backbone arm requires protic solvents and an additional ancillary ligand like benzonitrile or benzophenone. The resulting dearomatized iron hydride complex rapidly adds dihydrogen to a rearomatized *trans*-dihydride complex. These results led to a proposed all-iron(II) inner-sphere mechanism (Scheme 16) via substrate coordination (**A**→**B**), migratory insertion (**B**→**C**), metal-ligand cooperative H_2 -heterolysis (**C**→**D**) and product elimination (**D**→**A**).

Table 1. Catalytic hydrogenation of benzaldehyde with the iron PNP pincer precatalysts **Fe-1c** and **Fe-1d**.^{107,409,410}

pre-catalyst	precatalyst loading (mol%)	<i>T</i> (°C)	<i>p</i> (H_2)	additive	yield (%)	TON / TOF (h^{-1})	ref.
Fe-1c	0.125	RT	4.1 atm	0.1 mol% KOtBu	36	288 / 12	[107]
Fe-1d	0.05	40 °C	4.1 atm	0.8 mol% KOtBu	15	300 / 50	[409]
Fe-1c	0.025	40 °C	30 atm	0.625 mol% KOtBu xs. NEt_3	99	4000 / 250	[410]

This mechanism was later challenged by Yang within a DFT study on a PMe_2 -truncated model system.⁴¹¹ The author proposes the *trans*-dihydride complex $[(\text{PN}^{\text{Py}}\text{P})\text{Fe}(\text{H})_2\text{CO}]$ (**Fe-1e**) as the active catalyst species that reduces the substrate by outer-sphere hydride transfer. Importantly, the relevance of metal-ligand cooperation for catalysis was dismissed. Furthermore, EtOH solvent catalyzed H_2 heterolysis via an iron(II) ethanolate complex was proposed to accelerate dihydrogen activation.

Figure 29. Ketone and aldehyde hydrogenation precatalysts with diphosphinopyridyl and related ligands.

Scheme 16. Proposed MLC-assisted mechanism for the hydrogenation of ketones with iron P^{Ph}NP pincer catalysts.¹⁰⁷

In response, Milstein and co-workers pointed out that the *in situ* generated *trans*-dihydride **Fe-1e** does not react with acetophenone over an extended timescale in the absence of H₂ and therefore dismissed its relevance for catalysis.⁴⁰⁹ An alternative iron(II)/iron(0) cycle based on the full DFT model with explicit participation of the solvent (EtOH) as proton shuttle was proposed (Scheme 17). Rearomatization of the iron(II) hydride **A** was described as reductive elimination giving the four-coordinate iron(0) species **F**. After coordination of ethanol (**G**), concerted 2-proton/2-electron transfer from the pincer backbone and coordinated ethanol to the substrate restores iron(II) as the dearomatized ethanolate

complex **I**. Regeneration of parent **A** was proposed to proceed by hydrogenolysis of the iron ethanolate moiety via the two possible configurations of the dihydrogen intermediate (**J/L**) with low barriers and overall energetic span for the full cycle of 21.7 kcal·mol⁻¹.

Morello and Hopmann recently reevaluated these mechanisms computationally (full model, dispersion correction, PCM solvation model, one explicit EtOH as proton shuttle).⁴¹² The authors considered the solvent-assisted iron(0)/iron(II) redox cycle (Scheme 18, a) and three all-iron(II) mechanisms via the originally proposed active monohydride catalyst (Scheme 18, b), Yang's dihydride pathway without metal-ligand cooperativity (Scheme 18, c) and a dihydride route with pincer assisted H₂-heterolysis and proton shuttling (Scheme 18, d). The Fe(II)/Fe(0) mechanism (path a) was dismissed based on the high computed effective barrier for reductive elimination (52.5 kcal·mol⁻¹ or 37.5 kcal·mol⁻¹ with proton shuttling). Similarly, path b exhibits high effective barriers for the inner-sphere hydride transfer (38.0 kcal·mol⁻¹ for acetophenone) and subsequent proton transfer (32.9 kcal·mol⁻¹). Finally, mechanisms c (20.4 kcal·mol⁻¹) and d (20.1 kcal·mol⁻¹) are close in effective barrier. Notably, the scenario with the most favorable energy profile (d) combines Milstein's original proposal (metal-ligand and cooperative H₂ activation) with Yang's modification (dihydride catalyst with outer-sphere substrate activation).

Scheme 17. Proposed iron(II)/iron(0) redox mechanism for the acetophenone hydrogenation ($P = \text{P}i\text{Pr}_2$).⁴⁰⁹

Scheme 18. Computationally evaluated mechanisms for ketone hydrogenation with $\text{Fe}(\text{PN}^i\text{P})$ catalysts.⁴¹²

a) Redox-active dearomatization/aromatization pathway

b) Non-redox monohydride pathway

c) Non-redox dihydride pathway without dearomatization/aromatization

d) Non-redox dihydride pathway with dearomatization/aromatization

Milstein and coworkers reported the synthesis of precatalyst **Fe-21**, with an unsymmetrical PNN pincer ligand (Scheme 19).⁴¹³ Acetophenone and some mostly aliphatic ketones are reduced with low catalyst loadings and pressures. The relatively high loadings of the strong base $\text{KN}(\text{SiMe}_3)_2$ required

the use of THF as solvent. A strong dependence of the TON on the base/catalyst ratio was reported.

Scheme 19. Acetophenone hydrogenation with precatalyst **Fe-21**.⁴¹³

Precatalyst **Fe-22a** (Scheme 20) was investigated in the catalytic hydrogenation of ketones.⁴¹⁴ Similar substrate scope, yet lower activity was obtained in comparison to **Fe-1c**. While acetophenone was hydrogenated quantitatively (0.5 mol% **Fe-22a**; 1 mol% $\text{KO}t\text{Bu}$; 5 atm H_2 ; EtOH; r.t.), low yields were obtained for aliphatic and α,β -unsaturated ketones. No catalytic activity in ketone hydrogenation was obtained for the analogous *N*-methylated complex, suggesting the relevance of metal-ligand cooperativity.

Scheme 20. Ketone hydrogenation with catalyst **Fe-22a**. a: Yields were determined by NMR spectroscopy.⁴¹⁴

Stoichiometric control experiments in aprotic solvents revealed that formation of the *in situ* generated *cis*- and *trans*-dihydrides do not react with PhC(O)Me. Furthermore, the dihydrides are not formed in EtOH, highlighting the role of the solvent in stabilizing the dearomatized state. Based on these findings, an inner-sphere all-iron(II) monohydride pathway was proposed (Scheme 21, a).⁴¹⁴ However, Morello and Hopmann computed a high effective barrier for this mechanism (32.7 kcal·mol⁻¹ for PhC(O)Me) and favored a dihydride mechanism (Scheme 21, b) with much lower effective barrier (20.2 kcal·mol⁻¹).⁴¹² As for the PN^{Pr}₃P catalyst, acetophenone insertion into a Fe–H bond was computed to be slightly endergonic, in line with the stoichiometric control experiments in both cases.^{409,414}

Scheme 21. Computed pathways for ketone hydrogenation catalyzed by the Fe(PN₃P) platform.⁴¹⁴

a) Non-redox monohydride pathway

b) Non-redox dihydride pathway with dearomatization/aromatization

A modified PN₃P framework with axially chiral phosphoryl substituents were reported by Kirchner's group (Scheme 22). The iron precatalyst **Fe-22b** was directly used as an inseparable mixture of two diastereomers in the hydrogenation of acetophenones with good activity at mild conditions.⁴¹⁵

Scheme 22. Hydrogenation of acetophenones with precatalyst **Fe-22b**. Yields were determined by ¹H NMR spectroscopy.⁴¹⁵

In comparison to ketones, aldehyde hydrogenation with precatalyst **Fe-22a** exhibits low TON. Full conversion of aromatic and secondary aliphatic aldehydes was obtained with 5 mol% catalyst loading and good TOF (ca. 100 h⁻¹) at mild

reaction conditions (5 atm H₂, r.t., < 20 min; Table 2).⁴¹⁴ In contrast to picolinaldehyde, isonicotinaldehyde hydrogenation was inhibited by substrate coordination to the catalyst.

Table 2. Hydrogenation of aldehydes with catalyst **Fe-22a**.⁴¹⁴

Fe-22a

residue	yield [%]	TOF [h ⁻¹]
R = Ph	99	120
R = Cy	99	60
R = 2-Pyridyl	99	120
R = 4-Pyridyl	0	0

In a subsequent study, Gorgas et al. investigated the backbone *N*-methylated complex **Fe-22Me**.⁴¹⁶ This precatalyst exhibits exceptionally high activity in the hydrogenation of 4-fluorobenzaldehyde (TON_{Max} = 80000; TOF_{Max} = 20000 h⁻¹), exceeding the activity of parent **Fe-22a** by several orders of magnitude (Scheme 23). Another interesting feature is the high chemoselectivity with respect to aldehyde reduction vs. ketones, esters and olefins. Since a metal-ligand cooperative pathway is not possible, the authors proposed a dihydride mechanism for this catalyst.

In their comprehensive computational study, Morello and Hopmann examined the origin of the exceptional chemoselectivity of **Fe-22Me** in comparison with **Fe-1c** and **Fe-22a**, respectively.⁴¹² As proposed by Kirchner, the data support a dihydride mechanism without de-/aromatization for **Fe-22Me** (Scheme 18, c) in contrast to **Fe-1c** and **Fe-22a** (pathway d). The shift in mechanism is associated with different turnover determining intermediates (TDI) and transition states (TDTS).⁴¹⁷ In case of pathway d, the TDI (iron(II) alkoxide state) and TDTS (H₂ heterolysis) exhibit similar substrate dependence, resulting in about the same energetic span for (unselective) hydrogenation of different substrates. In contrast, pathway c features the dihydride resting state as TDI and the H₂ binding step as TDTS. It is evident that in this case the TDI is substrate independent while the Fe⁺/alkoxide⁻ ion-separated TDTS correlates with the product pK_a, which results in strong substrate discrimination. Hence, the selectivity is quenched if the resting state and the step with highest kinetic barrier share a linear free energy relationship for different substrates.⁴¹⁸ Given that the TDTS is often a substrate transformation step, a general guideline to achieve (chemo)selectivity can be to avoid the overstabilization of the substrate-bound ground states.

Scheme 23. Hydrogenation of 4-Fluorobenzaldehyde with PN_3P Iron Catalyst **Fe-22Me**.⁴¹⁶

The PN_3P pincer ligated manganese tricarbonyl complex **Mn-22a** was utilized by Sortais and coworkers for the catalytic hydrogenation of ketones (Scheme 24).⁴¹⁹ Stoichiometric NMR experiments revealed the formation of a manganese(I) hydride in the presence of H_2 and base, which requires CO dissociation, in contrast to Kempe's previously reported PN_5P based dicarbonyl manganese precatalyst (see below).⁴²⁰ Accordingly, the catalytic activity is inferior and prolonged reaction times are required for **Mn-22a**, despite high catalyst loadings, H_2 pressures and temperatures.

Scheme 24. Hydrogenation of acetophenone with precatalyst **Mn-22a**.⁴¹⁹

As an alternative, Kirchner and co-workers directly used the manganese dicarbonyl hydride complex **Mn-22b** as catalyst (Scheme 25).⁴²¹ The authors found pronounced chemoselectivity towards aldehydes. Turnover numbers up to 10400 were achieved for 4-fluorobenzaldehyde hydrogenation. Remarkably low catalyst loadings (0.05 – 0.1 mol%) can be used to reduce a broad range of aldehydes under 49 atm H_2 in ethanol, including α,β -unsaturated and aliphatic aldehydes.

Scheme 25. Hydrogenation of aldehydes with precatalyst **Mn-22b** (a: Yields determined by ^1H NMR spectroscopy).⁴²¹

Stoichiometric experiments revealed, that **Mn-22b** reacts with aldehydes and not with 4-fluoroacetophenone in both protic and nonprotic solvents. The alkoxide products do not undergo hydrogenolysis. The two main mechanisms that

were discussed for the iron pincer platforms, i.e. outer-sphere substrate insertion followed by H_2 heterolysis either with (Scheme 18, d) or without (Scheme 18, c) pincer ligand cooperativity, were also evaluated computationally for **Mn-22b** (Scheme 26).⁴²¹ Almost identical overall effective barriers ($\Delta\Delta G^\ddagger = 1 \text{ kcal mol}^{-1}$) were obtained for the two scenarios. The alkoxide represents the TDI for both routes, while the substrate is only involved in the TDTS of the non-MLC route. The MLC-pathway might therefore be better suited to explain the high chemoselectivity for aldehydes vs. ketones, which should be addressed in future studies. Notably, the respective manganese hydrides with NMe and CH_2 backbone linkers showed no (NMe) or poor (CH_2) activity further supporting a metal-ligand cooperative mechanism.

Scheme 26. Proposed Mechanism for the aldehyde hydrogenation with precatalyst **Mn-22b** ($\text{P} = \text{P}i\text{Pr}_2$).⁴²¹

Kempe and coworkers introduced the PN_5P pincer ligand platform with a triazine core for manganese catalyzed hydrogenation (Scheme 27).⁴²⁰ The manganese dicarbonyl complex **Mn-23** is a highly efficient catalyst for the hydrogenation of a vast range of aromatic and aliphatic ketones at milder reaction conditions compared with Beller's aliphatic precatalyst **Mn-15a** (Scheme 27). Benzaldehyde is quantitatively hydrogenated at mild conditions (0.1 mol% **Mn-23**, 40 °C).

Scheme 27. Hydrogenation of Ketones with the precatalyst **Mn-23** (a: Yields determined by GC and isolation).⁴²⁰

The same group employed the **PNsP** cobalt dichloride complex **Co-23a** as precatalyst for the catalytic hydrogenation of ketones and aldehydes (Scheme 28).⁴²² 24 ketones and aldehydes were reduced in predominantly very good yields applying 20 atm H₂ at room temperature with catalyst loadings ranging from 0.25 mol% to 3 mol%. Conjugated and remote C=C double bonds were retained in the catalytic experiments, which reflects the inverse selectivity in comparison to the aliphatic amino pincer catalyst reported by Hanson and coworkers (see below).¹⁹⁵ The authors propose the formation of a coordinatively unsaturated active cobalt(II) catalyst with a dianionic pincer ligand upon activation of **Co-23a** with two equivalents of NaOtBu, from trapping with bipyridine.

Scheme 28. Hydrogenation of ketones and aldehydes with precatalyst **Co-23a** (a: Yields determined by GC).⁴²²

3.1.2. Dialkylamino Pincer Catalysts Morris and co-workers introduced several iron precatalysts with aliphatic PNP pincer ligands for the catalytic hydrogenation of ketones with low catalyst loadings (0.2 mol%) in THF (Table 3), including asymmetric hydrogenation (see below).⁴²³ The achiral catalysts **CyFe-15b** and ***i*PrFe-15b** exhibit high activities in acetophenone hydrogenation (TOF = 1980 h⁻¹) at 50 °C and good activity at r.t. for precatalyst ***i*PrFe-15b** (TOF = 990 h⁻¹). Activation of the imine precatalysts requires addition of lithium aluminium hydride (LAH) and *tert*-amyl alcohol, respectively. A stoichiometric control experiment with excess LAH indicated the formation of an

iron(II) monocarbonyl hydride complex, [FeH(CO){H₃AlN(CH₂CH₂PCy₂)(CH₂CH₂PPh₂)}], i.e. an alane adduct of the hydride amide catalysts directly used by other groups (see below). Accordingly, alcoholysis produces an alkoxide hydride complex that is also an intermediate in the proposed catalytic cycles.

Table 3. (Asymmetric) Hydrogenation of ketones with the precatalysts **CyFe-15b**, ***i*PrFe-15b**, **Ph₂*i*PrFe-15b** and **Fe-15c** (deviation from standard conditions: a: 0.1 mol% **Fe-15c**, 1.0 mol% KOtBu, 6 eq. LiAlH₄; b: 0.1 mol% **Ph₂*i*PrFe-15b**, 1.0 mol% KOtBu, xs. LiAlH₄, 10 atm H₂, *t*AmOH/THF).⁴²³

substrate	catalyst	t [min]	conv. [%]	ee [%]	TON	TOF [h ⁻¹]
	CyFe-15b	15	99	-	495	1980
	<i>i</i>PrFe-15b	15	99	-	495	1980
	Fe-15c^a	30	99	80 (S)	990	1980
	Fe-15c^a	1440	0	n/a	0	0
	Fe-15c^a	240	95	0	950	240
	Fe-15c^a	48	99	85 (S)	990	1230
	Ph₂<i>i</i>PrFe-15b^b	150	90	-	900	360

CyFe-15b P = PCy₂

***i*PrFe-15b** P = P*i*Pr₂

Fe-15c

Benzaldehyde hydrogenation with **Fe-15c** was obtained with 90% conversion within 2.5 hours (Table 3). Considerably higher dihydrogen pressures (10 atm) are required compared with pyridyl based pincer catalysts (see above).⁴²³

Jones, Schneider and coworkers reported the hydrogenation of ketones using the aliphatic iron PNP pincer catalyst ***i*PrFe-15a** at mild, base-free conditions in THF at 10 atm H₂ (Scheme 29).⁴²⁴ In comparison, catalytic reactions with pyridine-based catalysts **Fe-1c** and **Fe-1d** are usually carried out in alcoholic solvents (see above). High C=O chemoselectivity was obtained for the α,β-unsaturated ketone benzalacetone to the kinetic allyl alcohol product. Interestingly, the Jones group later reported the full hydrogenation of benzalacetone with the same catalyst in benzene, at higher catalyst loadings (5 mol %) and lower H₂ pressure (Scheme 72, section 3.7.2). NMR monitoring verified the allylic alcohol as the main intermediate. The apparent H₂ pressure dependence of the selectivity suggests that the full hydrogenation of benzalacetone might proceed via allyl alcohol isomerization

Figure 30. Ketone and aldehyde hydrogenation precatalysts with dialkylamino PNP and NNN pincer ligands.

(C=O dehydrogenation/C=C hydrogenation), which requires the amide catalyst state.

Scheme 29. Ketone hydrogenation catalyzed by complex **iPrFe-15a**.⁴²⁴

Accordingly, in the absence of H₂ the isomerization of allylic alcohols to ketones is catalyzed by the Fe(**iPrPN^HP**) catalyst platform (Scheme 30).⁴²⁵ A broad range of allylic alcohols were isomerized to the respective ketone with precatalyst **Fe-15d**/KO*t*Bu. In 2-propanol the fully reduced transfer hydrogenation product was mainly obtained. A ‘self-hydrogen-borrowing’ mechanism was proposed based on control experiments and DFT calculations (Scheme 30), which is discussed in detail in Section 5. After AAD of the allylic alcohol the α,β-unsaturated ketone is rehydrogenated either by 1,4-addition or 1,2-addition, which both give the ketone after vinylalcohol tautomerization. 1,4- and 1,2-addition exhibited similar kinetic barriers by DFT.

Scheme 30. (a) Catalytic Isomerization of Allylic Alcohols with Iron PNP Pincer Complex **Fe-15d**. (b) Proposed Self-Hydrogen Borrowing Mechanism for the Isomerization of Allylic Alcohols Catalyzed by Iron Pincer Complexes (P = P*i*Pr₂).⁴²⁵

Hanson and coworkers established a versatile cobalt catalyst for the hydrogenation of C=C, C=O and C=N double bonds at mild conditions, which is discussed in detail in Sections 3.7.1. and 3.2, respectively. The square-planar, low-spin cobalt(II) pincer precatalyst **Co-7** was used, which requires activation with Brookhart's acid [H(Et₂O)₂]BAR^F₄ (Scheme

31).¹⁹⁵ The activated precatalyst was crystallographically characterized. However, the structural features shed doubt on the assignment as the *N*-protonated complex $[(^{\text{C}}\text{P-N}^{\text{H}}\text{P})\text{Co}^{\text{II}}(\text{CH}_2\text{SiMe}_3)]\text{BAR}^{\text{F}_4}$ (**Co-15b**).¹⁹⁵ The almost planar coordination environment around the nitrogen donor and alternating C–N bond lengths (1.38/1.45 Å) in the pincer backbone suggest formation of an imine species upon protonation. Interestingly, the corresponding tetraphenylborate salt (from protonation of **Co-15a** with $[\text{HNEt}_3]\text{BPh}_4$) features different backbone metrics (1.48/1.50 Å) and exhibits considerably lower activity in acetophenone hydrogenation.⁴²⁶ The ambiguity regarding the activated precatalyst species requires further clarification.

Scheme 31. Hydrogenation of C–O, C–C and C–N double bonds with precatalyst **Co-15a**.¹⁹⁵

The high activities for both unactivated olefins and carbonyl groups are rather unusual for catalysts with this ligand. In comparison, the iron(II) amide catalyst **Fe-15a** generally exhibits C=O over C=C chemoselectivity and preferentially reduces activated, electron deficient olefins.¹⁹⁶ For the iron catalyst, this is attributed to an outer-sphere mechanism, as discussed above and in Section 3.7. In contrast, cobalt catalyzed olefin hydrogenation was proposed to operate via inner-sphere olefin insertion at the cobalt(II) hydride $[(^{\text{C}}\text{P-N}^{\text{H}}\text{P})\text{CoH}]^+$, which is discussed in Section 3.7.2.^{195,426} For ketone hydrogenation, the redox states of the active cobalt species remain unclear. From reverse, acceptorless alcohol dehydrogenation, a cobalt(III) complex could be isolated but

it exhibits much lower catalytic activity in ketone hydrogenation than parent **Co-15a**/[H(Et₂O)₂] BAR^{F_4} .⁴²⁶ Furthermore, the *N*-methylated precatalyst $[(^{\text{C}}\text{P-N}^{\text{Me}}\text{P})\text{Co}^{\text{II}}(\text{CH}_2\text{SiMe}_3)]\text{BAR}^{\text{F}_4}$ (**Co-15Me**) is not active in acetophenone hydrogenation suggesting the relevance of MLC.

Hanson's catalyst was also used as catalyst for transfer hydrogenation of C–O and C–N double bonds.⁴²⁷ With *iso*-propanol/THF as solvent and hydrogen source, 13 ketones and aldehydes and 3 imines were reduced under mild conditions (2 mol% @ 25 °C for 24 h; Imines: 80 °C). Deuteration experiments favor a monohydride over dihydride mechanism.⁴²⁸ The *N*-methylated pincer complex **Co-15Me** exhibits only slightly reduced activity in acetophenone hydrogenation, suggesting that MLC is irrelevant for catalysis. Furthermore, the lack of chemoselectivity for transfer hydrogenation of α,β -unsaturated substrates contrasts with related iron-systems, and was rationalized with an inner-sphere mechanism for the cobalt catalyst.

Scheme 32. Hydrogenation of ketones, aldehydes and nitriles with precatalyst **ⁱPrMn-15a** (a: 30 atm H₂, 100 °C; b: Yields determined by GC).⁴²⁹

The Beller group introduced **ⁱPrMn-15a** (Scheme 32) as the first manganese precatalyst for the hydrogenation of polar multiple bonds.⁴²⁹ A broad range of aromatic and aliphatic ketones, aldehydes and nitriles are hydrogenated in moderate to quantitative yields using 1-3 mol% catalyst and 3-10 mol% base (NaOtBu) loadings under harsher conditions (10-49 atm H₂; 60-100 °C; 24-60 hours) as compared with the

ASYMMETRIC KETONE HYDROGENATION

Figure 31. Summary of asymmetric ketone hydrogenation catalysts based on tridentate PNP and PNN Ligands (P* = Pdmp; dmp = (2*R*,5*R*)-2,5-dimethylphospholane).

analogous iron system. Unpolar (C=C) double bonds are tolerated, as well as potentially coordinating substrates like 3-acetylpyridine. The almost quantitative yield of the cyclopropyl-substituted ketone precludes a reaction mechanism that proceeds via stable radical intermediates.

¹H NMR and IR spectroscopic examination revealed hydride formation *trans*-positioned to a CO ligand upon reaction of *i*PrMn-15a with dihydrogen and NaOtBu. In analogy to related iron-systems the catalytically active species are proposed to be manganese amine-hydride and amide complexes. DFT computations indicated almost thermoneutral H₂ 1,2-addition to the amide (*i*PrPNP)Mn(CO)₂. A related catalyst was described by Sortais and coworkers for the hydrogenation of ketones.⁴³⁰ In contrast to the corresponding rhenium system, the manganese bis(phosphinite) pincer precatalyst (1 mol%) exhibits 25% conversion in acetophenone hydrogenation. Interestingly, the backbone methylated analogous complex showed only slightly lower conversion (20%).

Scheme 33. Transfer hydrogenation of acetophenone with precatalyst **Mn-24** (a: Yield determined by GC).⁴³¹

Beller and co-workers also reported catalytic transfer hydrogenation of ketones with Mn dipyriddy amine pincer complex **Mn-24** (Scheme 33).⁴³¹ *i*PrOH was used as hydrogen source at 80 °C over the course of 24 hours with 1 mol% catalyst loading and 2 mol% base (KOtBu). A broad range of ketones was hydrogenated in moderate to almost quantitative yields. The authors found comparable catalytic activity with the analogous *N*-methylated backbone precursor, suggesting that pincer-mediated, metal-ligand cooperative H₂-activation is not a general prerequisite.

In summary, iron pincer catalysts are more active than manganese and significantly more active than cobalt pincer

catalysts in the hydrogenation of ketones and aldehydes with the same or similar ligand platform (Figure 30). Catalysis in the low digit ppm range is currently only possible with iron pincer catalysts at mild reactions conditions. However, the pool of manganese pincer catalysts is rapidly growing.

Figure 32. Asymmetric transferhydrogenation of acetophenone with tetradentate PNNP Fe(II) catalysts.^{432–434}

3.1.3. Asymmetric Hydrogenation of Ketones.

Seminal contributions to iron catalyzed asymmetric transfer hydrogenation (ATH) were made by the Morris group using tetradentate PNNP ligands that are closely related to aforementioned pincer platforms.⁷⁷ Three catalyst generations were reported based on rational ligand design (Figure 32). First generation catalysts with rigid ligand backbone exhibit high TOF (1632 h⁻¹) and medium enantioselectivity (63 % ee) in acetophenone ATH.⁴³² The more flexible second generation ligand gave strongly improved TOF (26000 h⁻¹) and enantioselectivity (90 % ee),⁴³³ while 3rd generation catalysts exhibit extraordinary activities (TOF = 547200 h⁻¹), albeit with reduced selectivity (70 % ee).⁴³⁴ Apparently the combination of imine and amine donors is mandatory since the respective diamine complexes were inactive in ATH. Mechanistic investigations and ligand variations with respect to the backbone and phosphorus substituents gave additional insight.^{435–437} While considerably more active than iron pincer catalysts, the PNNP systems are prone to reduced stereoselectivity due to racemization of the product alcohol.

Scheme 34. Asymmetric ketone hydrogenation with precatalyst **Fe-15e** (a: Conversion and *ee* determined by chiral GC).⁴³⁸

The chiral PNP catalyst **Fe-15c** (Table 3, Figure 31) was used for asymmetric hydrogenation by the Morris group as an extension of their PNNP-based catalysts.⁴²³ High catalytic activities and up to 85 % *ee* were obtained for a range of prochiral ketones. The hydrogenation of a α,β -unsaturated ketone was chemo- but not stereoselective, while an α,β -unsaturated ketone was not hydrogenated. The highest enantioselectivities in asymmetric hydrogenation of aromatic ketones with iron pincer catalysts to date were obtained using the second generation catalyst **Fe-15e** (Scheme 34).⁴³⁸ For aliphatic methyl ketones, high conversion but low *ee* was observed in case of 3-methylbutanone and no conversion for the bulkier substrate 3,3-dimethylbutanone.

Scheme 35. Asymmetric hydrogenation of acetophenone with precatalyst **Fe-1f**.⁴⁴⁰

The dependence of activity and stereoselectivity on the ligand backbone substitution pattern was examined by systematic screening of a ligand library.⁴³⁹ The highest activities are obtained with CHMe or CH₂ group next to the central nitrogen donor. In turn, the best enantioselectivities are achieved with a CHPh group next to PPh₂ donor, which was rationalized with the subtle interplay of pincer backbone rigidity for stereoselectivity and accessibility of the amine functional group for high reaction rates.

Scheme 36. Asymmetric hydrogenation of acetophenone with precatalyst **Fe-25**.⁴⁴¹

A pyridine-based iron catalyst with chiral phosphine substituents was also reported (Scheme 35).⁴⁴⁰ Precatalyst **Fe-1f**

requires comparatively high pressures and catalyst loadings. Furthermore, low enantioselectivity was found. Importantly, evaluation of the mechanism by means of DFT revealed that only an outer-sphere mechanism with metal-ligand cooperation could reproduce the experimentally observed product stereoselectivity.

Scheme 37. Asymmetric transfer hydrogenation of ketones with precatalyst **Mn-25**.⁴⁴²

The introduction of a ferrocenyl-bridged pincer backbone was described by Kirchner, Morris and coworkers (Scheme 36).⁴⁴¹ Enantiomeric excess up to 81% was obtained at relatively high dihydrogen pressure (20 atm) and catalyst loadings (1 mol% **Fe-25**). Kirchner and coworkers also utilized this ligand for manganese-catalyzed ATH of ketones (Scheme 37).⁴⁴² The chiral catalyst **Mn-25** gave up to 85 % *ee* for acetophenone with iPrOH as hydrogen donor. Addition of gaseous H₂ did not affect the yield. Upon reaction of **Mn-25** with KOtBu in iPrOH two isomeric monohydride complexes are formed and proposed as active species. The authors attributed the *S*-selectivity to the steric repulsion and stabilizing hydrogen bonding of the substrate with the pincer backbone.

Clarke and coworkers utilized the tricarbonyl complex **Mn-26** with a chiral, facially coordinating PNN ligand as the first manganese precatalyst for the asymmetric hydrogenation of ketones (Scheme 38).⁴⁴³ A range of 18 aromatic substrates were hydrogenated in moderate to excellent yields. Enantioselectivity showed a strong dependency on the substrate sterics. Enantiomeric excess beyond 80% was generally obtained with arylketones ArC(O)R that carry secondary and tertiary substituents. High yield but low *ee* were obtained for ATH with iPrOH as hydrogen donor. While the mechanism was not explicitly examined, the authors propose MLC, in analogy to Beller's system.

Figure 33. Summary of imine and *N*-heterocycle hydrogenation catalysts based on tridentate PNP Ligands.

Scheme 38. (Asymmetric) hydrogenation of ketones and esters with precatalyst **Mn-26**.⁴⁴³

As an extension to their {Mn(PNP)} catalyst platform **Mn-15a**, the Beller group examined asymmetric ketone hydrogenation with the chiral catalyst **dmpMn-15b** (Scheme 39).⁴⁴⁴ In this case, chiral induction is achieved using (2*R*,5*R*)-2,5-dimethylphospholane substituents. A range of aromatic and also aliphatic ketones were hydrogenated in moderate to good enantioselectivities at 40 °C and 30 atm H₂ pressure. In contrast to Clark's catalyst **Mn-26**, this system preferentially catalyzes the hydrogenation of aliphatic ketones with high enantioselectivity.

Scheme 39. Asymmetric hydrogenation of ketones with precatalyst **dmpMn-15b**.⁴⁴⁴

The authors proposed catalyst activation by CO dissociation and formation of a monohydride-amine catalyst. DFT calculations indicate highly unfavorable dissociation of a second CO ligand (>42 kcal·mol⁻¹), and facile H₂ elimination ($\Delta G^\circ = +1$ kcal·mol⁻¹; $\Delta G^\ddagger = 20$ kcal·mol⁻¹) from a hydride-amine complex, in agreement with the high required pressures. Based on the theoretical model a concerted, outer-sphere MLC-mechanism was proposed via hydride-amine and amide species. The model predicted the correct enantioselectivities but overestimated the barriers for dihydrogen transfer to the substrate (30-36 kcal·mol⁻¹).

3.2. Hydrogenation of Imines and *N*-Heterocycles

The chiral complex **Fe-15c** is an excellent catalyst for the asymmetric hydrogenation of the activated imine *N*-(diphenylphosphanyl)propiophenoneimine (Scheme 40).⁴²³ The stereoselectivity (90 % ee) is lower compared with the Fe(PNP) catalyst developed by the same group but higher than for an iron catalyst previously reported by Beller and coworkers.^{445,446} Related hydride precatalyst **Fe-15f** catalyzes the hydrogenation of (iso)quinolines, indoles and pyridines in moderate to good yields at mild conditions (Scheme 40).¹⁸⁰ A hydride-amine/amide MLC pathway was proposed.

Scheme 40. Hydrogenation of *N*-heterocycles and imines with Iron and cobalt PNP pincer complexes.^{180,195,423}

Cobalt catalyzed imine hydrogenation (Scheme 40) has been reported with Hanson's catalyst **Co-15b**.¹⁹⁵ Jones and coworkers further expanded the substrate scope for a range of *N*-heterocycles in THF at 120 °C (5 mol% catalyst loading, 10 atm H₂).⁴⁴⁷

3.3. Hydrogenation of Amides

Amide hydrogenation to the respective amines and alcohols was first described with an iron pincer catalyst by Milstein and coworkers.⁴⁴⁸ The **PN^{Py}P** iron complex **Fe-1c** catalyzes the hydrogenation of activated, electron deficient amides at high temperatures and pressure with comparably high catalyst loadings (Scheme 41). The strong base KN(SiMe₃)₂ (KHMDs), rather than more common KO^tBu, was used for activation of **Fe-1c** enabling the hydrogenation of twelve trifluoroacetamides. The borohydride complex **Fe-1d** exhibits slightly lower activity, yet does not require addition of base like **Fe-1c**. A mechanism via a hemiaminal intermediate was proposed, in analogy to ester hydrogenation, which is discussed in Section 3.5.⁴⁴⁹

Scheme 41. Amide hydrogenation with precatalyst **Fe-1c**.⁴⁴⁸

Langer and coworkers first reported iron pincer catalyzed hydrogenation of non-activated amides,¹⁸⁵ using **EtFe-15g** as catalyst. The sterically less demanding PEt₂-ligand had been previously shown to be more efficient in ester hydrogenation than the popular ligands **RPNH^{Pr}P** (R = *i*Pr, Cy).⁴⁵⁰ Nine different amides and lactams were hydrogenated under base-free conditions at milder conditions and lower catalyst loadings than with pyridyl pincer complex **Fe-1c**. However, most lactams required harsh conditions and high catalyst loading.

In a consecutive study, Sanford and coworkers compared the activities of (**RPNH^{Pr}P**)Fe(BH₄)(H)(CO) (R = Et, Cy, *i*Pr) in amide hydrogenation with additional K₃PO₄ as base for catalyst activation.⁴⁵¹ In fact, **CyFe-15g** exhibited the best performance while **EtFe-15g** was by far inferior. Strong advantages of Sanford's protocol are the relatively low precatalyst loadings (0.33 mol%) and moderate H₂ pressures (20 atm) needed for formamide hydrogenation. Interestingly, reproducibility of the catalytic rates required the use of research grade H₂ (99.9999%).

Table 4. Hydrogenation of amides with iron precatalysts **EtFe-15g** and **CyFe-15g**.^{185,451}

amide	Fe-precatalyst	additive	<i>p</i> (H ₂) [atm]	<i>T</i> [°C]	<i>t</i> [h]	yield (alc./amine) [%]
Ph-C(=O)-N(Ph)Ph	EtFe-15g 2 mol%	---	49	100	24	99 / 99
Ph-C(=O)-N(Ph)Ph	CyFe-15g 4 mol%	20 mol% K ₃ PO ₄	49	130	3	95
CF ₃ -C(=O)-N(Ph)Ph	EtFe-15g 10 mol%	---	49	100	24	92
F ₃ C-C(=O)-N(Ph)Ph	EtFe-15g 2 mol%	---	49	70	24	n.d. / 99
H-C(=O)-NPh ₂	CyFe-15g 0.33 mol%	1.66 mol% K ₃ PO ₄	20	110	3	99

Jayarathne *et al.* employed the related amide complex ***i*PrFe-15a** for the hydrogenation of (form)amides with a very low catalyst loading of 0.07 mol% (Scheme 42).⁴⁵² Turnover numbers up to 5600 could be obtained. Interestingly, the authors found the addition of an excess *N*-phenylformamide significantly increased the yield and therefore the turnover number (Scheme 42). Subsequent mechanistic examinations attribute this effect for *N,N*-disubstituted amide substrates to metal-free, organocatalytic cleavage of the hemiaminal intermediate to formaldehyde and secondary amines.⁴⁵³ In consequence, initial outer-sphere hydride transfer to the amide substrate is the relevant step for catalyst design. Furthermore the influence of Lewis-acid additives was examined. Increased yield was observed upon addition of lithium triflate. The combination of both promoters leads to a nearly additive enhancement effect.

Scheme 42. Amide hydrogenation precatalyst ***i*PrFe-15a**.⁴⁵²

Beller and co-workers reported the catalytic upgrading of CO to ethylene glycol.⁴⁵⁴ The first step comprises palladium-catalyzed, aerobic coupling of CO and piperidine to the oxamide (C(O)NC₅H₁₀)₂. Catalyst screening (Ru and Fe) for subsequent hydrogenolysis of the amide intermediate gave high yields in ethylene glycol for **EtFe-15g** yet at higher

Figure 34. Summary of amide hydrogenation catalysts based on tridentate PNN and PNP ligands.

loadings of catalyst and base than for the related (**PhPN^HP**)Ru(BH₄)(H)(CO).

Scheme 43. Deoxygenative hydrogenation of amides catalyzed by **Mn-1a**.⁴⁵⁵

The pyridyl pincer manganese complex **Mn-1a** was employed in the deoxygenative hydrogenation of amides by Milstein and coworkers (Scheme 43).⁴⁵⁵ Stoichiometric amounts of Lewis acid additive B(C₆F₅)₃ increased the yield. Besides MLC H₂ heterolysis, the dearomatized manganese complex also forms a dinuclear N₂-complex.

Scheme 44. Amide hydrogenation with precatalyst **Mn-27**.⁴⁵⁶

Beller and coworkers introduced the PNN pincer manganese complex **Mn-27** into amide hydrogenation (Scheme 44). Isomerization to meridional chelation can be expected after CO dissociation. The catalytic protocol utilizes 2-4 mol%

Mn-27 and 10 mol% KO^tBu at 100 °C in cyclohexane under 30 atm H₂. A broad substrate scope of 25 (form)amides were hydrogenated in moderate to quantitative yields.

Scheme 45. Hydrogenation of nitriles by precatalyst **iPrFe-15g** (a: Isolated as well as GC yields).⁴⁵⁷

3.4. Hydrogenation of Nitriles

A comprehensive study on iron catalyzed nitrile hydrogenation was reported by Beller and coworkers in 2014 (Scheme 45).⁴⁵⁷ Borohydride complex **iPrFe-15g** represented the first non-precious metal catalyst for nitrile hydrogenation to the respective ammonium salts after acidic workup. A vast range of (di)nitriles were converted in *i*PrOH as solvent without need for additional base giving moderate to almost quantitative amine yields. Excellent functional group tolerance was obtained for 24 aromatic nitriles and even 12 aliphatic nitriles which were reduced at relatively mild conditions and low catalyst loadings. Several aromatic and aliphatic dinitriles, like the polyamide production intermediate hexanedinitrile, were also converted in moderate to very good yields. Based on DFT computations, an all-iron(II) hydride-amine/amide outer-sphere mechanism was proposed with almost thermoneutral H₂ addition to the iron amide state.^{457,458} Spectroscopic evidence for the iron(II) amide was presented, which could later be isolated by several groups.^{180,181} The relevance of MLC for catalysis is further supported by the lack of activity in case of the backbone *N*-methylated complex **iPrFe-15Me**. A comparative study on the catalyst series **RFe-15g** (R = Et, Cy, *i*Pr) revealed almost comparable nitrile hydrogenation activity for **CyFe-15g**.⁴⁵⁹

NITRILE HYDROGENATION

Figure 35. Summary of nitrile hydrogenation catalysts based on PNP and PNN pincer ligands.

Milstein and coworkers reported the reductive homocoupling of aromatic and aliphatic nitriles to secondary imines and ammonia, catalyzed by the unsymmetric pincer catalyst **Fe-28**/KOtBu (Scheme 46).⁴⁶⁰ Aromatic nitriles generally give higher yields with comparably lower catalyst loadings. Cross coupling to unsymmetrically substituted aldimines RHC=NR' can be achieved with the same catalyst starting from nitriles RCN and amines H₂NR', respectively, at considerably milder reaction conditions (1 mol% **Fe-28**/KOtBu, 10-20 atm H₂, 60 °C).⁴⁶¹ A range of 20 different aldimines was synthesized with a similar substrate scope compared to reductive nitrile homocoupling.

Scheme 46. Reductive coupling of nitriles to secondary imines catalyzed by **Fe-28**.⁴⁶⁰ (a: Yields determined by GC-MS and ¹H NMR spectroscopy).

The authors proposed a pathway via the condensation of primary imine and amine intermediates (Scheme 47). Spectroscopic examination revealed the formation of an iron(II) monohydride amide complex from reaction of **Fe-28** with base that adds H₂. In turn the resulting amine dihydride transferred H₂ to benzonitrile in a stoichiometric control experiment, reforming the amide species. These results support a MLC mechanism. Interestingly, a *cis*-dihydride configuration was found for the H₂-addition product which is the minor isomer in case of (iPrPNH₂P)Fe(H)₂CO.¹⁸¹ Evidently, secondary imine formation requires the accumulation of a primary imine intermediate. It is therefore tempting to correlate the different nitrile hydrogenation selectivities of the structurally strongly related catalysts to hydricities of *cis*- and *trans*-dihydride isomers.

Scheme 47. Proposed mechanism for iron PNP pincer catalyzed hydrogenation of nitriles to secondary imines (**P** = P(Pr)₂).⁴⁶⁰

The cobalt catalyst **Co-29** was utilized by Milstein and coworkers for the hydrogenation of 23 (hetero)aromatic, benzylic and aliphatic nitriles to primary amines (Scheme 48) at comparatively forcing conditions (135 °C, 30 atm H₂).⁴⁶² Catalyst (2 mol%) activation required 2 mol% NaBET₃H and 4.4 mol% NaOEt, respectively, as additives. Benzylic and aliphatic amines generally give lower yields. For pentanenitrile and heptanenitrile as substrates, secondary amines were observed, which is rationalized with reductive nitrile coupling as for the iron catalyst **Fe-28**,^{460,461} and subsequent hydrogenation of the secondary imine intermediate. The authors propose a monoanionic, dearomatized phosphinediamide cobalt(I) hydride complex as active catalyst species.

Scheme 48. Hydrogenation of nitriles catalyzed by precatalyst **Co-29**.⁴⁶²

Versatile, base-free transfer hydrogenation of nitriles with ammonia borane as the hydrogen source was described by

ESTER HYDROGENATION

Figure 36. Summary of Ester Hydrogenation Catalysts Based on Tridentate PNP and PNN Ligands.

the groups of Zhou and Liu utilizing related cobalt(II) PNN pincer precatalysts with divergent selectivities (Scheme 49).⁴⁶³ Transfer hydrogenation (TH) of nitriles to the respective primary amines is catalyzed by **Co-30** (1 mol%) in *n*-hexane at 50 °C. The substrate scope covered 26 (hetero)aromatic and aliphatic (di)nitriles. TH of aliphatic (di)nitriles requires elevated temperatures. In contrast, hydrogenative homocoupling to secondary amines is observed with precatalyst **Co-31** in (CF₃)₂CHOH as solvent. A range of 20 nitriles could be coupled via this methodology in moderate to good yields with high tolerance of reducible groups. Tertiary amines can be obtained from reductive cross-coupling of nitriles with a secondary amine. Pincer *N*-methylated analogs of the precatalysts did not significantly affect the yields suggesting an inner-sphere mechanism without MLC.

Scheme 49. Nitrile hydrogenation and hydrogenative coupling with precatalysts **Co-30** and **Co-31**.⁴⁶³

3.5. Hydrogenation of Esters

The iron pincer catalyzed hydrogenation of esters was first reported by Milstein and coworkers (Scheme 50).⁴⁴⁹ The pyridyl-pincer dihydride complex **Fe-1e** catalyzes the hydrogenation of activated trifluoroacetic esters in the presence of base (KO^tBu). A TON up to 1280 could be obtained for the hydrogenation of 2,2,2-trifluoroethyl trifluoroacetate. The authors suggested a mechanism that is related to their initial proposal for ketone hydrogenation via carboxylate insertion into a dihydride M-H bond and MLC H₂ heterolysis. Dissociation of the hemiacetal intermediate and subsequent trifluoroacetaldehyde hydrogenation were proposed as pathway to the final products.

Scheme 50. Hydrogenation of trifluoroacetic esters, bicarbonate and CO₂ with catalyst **Fe-1e**.^{241,449}

Shortly after, the groups of Beller and Guan independently reported the first examples for hydrogenation of nonactivated esters,^{182,458} while Hazari and Schneider described reverse acceptorless alcohol dehydrogenation to esters as discussed in Section 4.1.1.⁴²⁴ All groups used iron ⁱPrPN^HP-based catalysts. Beller and coworkers employed the borohydride complex ⁱPrFe-15g for ester hydrogenation under base-free conditions with high functional group tolerance at high H₂ pressure (30 atm) and temperature (100-120 °C) with 1 mol% catalyst loading (Scheme 51).⁴⁵⁸ Selective ester reduction was obtained for methyl-4-decenoate as substrate. In comparison, Guan's protocol requires higher loadings in ⁱPrFe-15g (3 mol%) yet at lower pressure (10 atm) and was also applied to a broad substrate scope,¹⁸² and subsequently to an industrially derived sample (CE-1295) on a kilogram scale.⁴⁶⁴ Starting from the backbone *N*-methylated complex ⁱPrFe-15Me no conversion of methyl benzoate was obtained suggesting the relevance of MLC.⁴⁵⁸ More detailed experimental and computational examinations were reported for reverse acceptorless alcohol dehydrogenation with this catalyst platform, which is discussed in Section 4.1.1.⁴²⁴ Beller and Langer independently reported improved catalytic activity for the sterically less encumbered ^{Et}Fe-15g (Scheme 51) allowing for reduction of the temperature 60-70 °C and pressure (10 atm) for reference substrate methylbenzoate.^{185,450}

Scheme 51. Hydrogenation of methylesters and lactones with (PN^H/MeP) iron precatalysts.^{185,450,458}

Expansion to manganese catalyzed ester hydrogenation was first reported by the Beller group.⁴⁶⁵ The manganese(I) precatalysts ***i*PrMn-15a** and **fac-EtMn-15b** (Scheme 52) exhibit comparable catalytic performance towards methyl benzoate. The authors propose formation of the same amido dicarbonyl complex, (EtPNP)Mn(CO)₂, upon activation with base as the catalytically active species. Isomerization of **fac-EtMn-15b** after deprotonation and CO dissociation to *mer*-(EtPNP)Mn(CO)₂ was computed to be exergonic by 7.7 kcal·mol⁻¹. A broad range of 27 esters was reduced with **fac-EtMn-15b**, including (hetero)aromatic as well as aliphatic esters and lactones. Remote C=C double bonds were retained under the catalytic conditions, while α,β-unsaturated esters were reduced to the saturated alcohols. Stepwise ester to alcohol reduction via a hemiacetal intermediate was proposed based on DFT computations. The highest barrier was obtained for the first outer-sphere hydride transfer reaction suggesting catalyst optimization based on Mn–H hydricities.

Scheme 52. Hydrogenation of esters using precatalysts **fac-EtMn-15b** and **EtMn-15a**, respectively (a: Isolated yields as well as yields determined by GC; b: identical result for **EtMn-15a**; c: 48 h; d: 3-phenylpropanol as product).⁴⁶⁵

The ketone hydrogenation precatalyst **Mn-26** (Scheme 38, Section 3.1.3.) is also active in the hydrogenation of esters with similar activities as Beller's manganese catalyst.⁴⁴³ A range of eight (di)esters were hydrogenated to the respective alcohols in moderate to quantitative yields at 75 °C over 18 h in *i*PrOH. Only the *para*-nitro derivative showed no conversion and aliphatic esters were hydrogenated with lower yields.

Scheme 53. A) Hydrogenation of esters and lactones with precatalyst **Mn-29a** (a: Yields determined by GC). B) Stoichiometric control experiments.⁴⁶⁶

The pyridine based PNN manganese complex **Mn-29a** (1 mol%) was used for reduction of 14 aromatic and aliphatic esters and lactones (100 °C, 20 atm H₂) with predominantly very good yields (Scheme 53).⁴⁶⁶ The catalyst is activated by the unusual base KH (2 mol%). Stoichiometric control experiments show that deprotonation of the secondary amine ligand is favored over dearomatization. The structurally characterized amido pincer complex **Mn-29b** reversibly splits dihydrogen by MLC to the amine monohydride complex **Mn-29c**. Based on these observations, the authors propose a catalytic cycle via outer-sphere hydrogenation and MLC H₂ heterolysis, emphasizing the relation to the aliphatic **RPN^HP**.

Milstein and co-workers introduced the cobalt PNN pincer complex **Co-29** for ester hydrogenation (Scheme 54).⁴⁶⁷ The electronic structure of **Co-29** was not reported but high-spin cobalt(II) can be expected based on M-L bond lengths. Upon activation with KO^tBu and sodium superhydride a range of 11 different esters could be reduced in moderate to good yields. Interestingly, the authors observed an unusual selectivity. The generally more challenging aliphatic ester substrates were converted in contrast to aromatic and activated trifluoroacetic acid esters. As an explanation, the authors propose a mechanism via initial ester enolization with the strong base KO^tBu and subsequent cobalt catalyzed C=C hydrogenation of the enolate. In consequence, benzoates and trifluoroacetic acid esters are not enolizable. This mechanism implies preferential C=C over C=O reduction by a cobalt hydride, as reflected by the milder conditions of alkene over ketone hydrogenation observed for Hanson's cobalt aminopincer system (Scheme 31).¹⁹⁵

Scheme 54. Hydrogenation of esters with precatalyst **Co-29**.⁴⁶⁷

Hanson's catalyst, **Co-15a**/[H(Et₂O)₂]⁺BAR^F₄⁻ (**Co-15b**), was also employed in ester hydrogenation by Jones and co-workers.⁴⁶⁸ Without further additives 11 substrates could be hydrogenated to alcohols, including aliphatic and aromatic esters with 2 mol% cobalt loading at 120 °C and 54 atm H₂ (Scheme 55). Interestingly, a pincer *N*-methylated analogous complex exhibited only slightly reduced catalytic activity. The authors therefore proposed an inner-sphere mechanism without MLC. However, as pointed out above there remains some ambiguity regarding the nature of Hanson's catalyst, which is discussed in Section 3.1.2.

Scheme 55. Hydrogenation of esters with Co(R^PN^HP) catalysts.^{197,468}

The hydrogenation of a broad range of 30 different esters was reported by Beller and coworkers starting from **PhCo-**

15c (5 mol%) and NaOMe (20 mol%) with predominantly good yields (Scheme 55).¹⁹⁷ The substrate scope includes many carbo- and heterocyclic, aliphatic and aromatic (di)esters as well as lactones. The authors note, that a black precipitate is observed at 140 °C after 24 hours attributed to cobalt nanoparticles. However, mercury and PMe₃ poisoning experiments were unsuccessful and the *N*-methylated pincer complex exhibited no activity in the hydrogenation of methyl benzoate and methyl octanoate.

3.6. Hydrogenation of CO₂

Several products can arise from CO₂ hydrogenation that range in principle from formic acid and CO (2-electron reduction), formaldehyde (4e⁻) and methanol (6e⁻) all the way to methane (8e⁻) or other hydrocarbons.⁴⁶⁹ Regarding the 2-electron products, formic acid or CO, both reactions are endergonic at ambient conditions in the gas phase. However, formic acid formation can be driven by product deprotonation in polar solvents. Besides this thermochemical argument, the reaction of transition metal hydrides with CO₂ usually leads to formates, which is therefore called the *normal insertion*, thereby determining formate selective catalysis.²⁰⁶ CO₂ hydrogenation in basic aqueous conditions is further complicated by substrate solvation and the nature of the true hydrogenated species, CO₂ or (bi)carbonate, is not always clear.

Scheme 56. Proposed mechanism for CO₂ hydrogenation with catalyst **Fe-1e** (P = PtBu₂).²⁴¹

3.6.1. Pyridyl-Based Pincer Catalysts First-row metal catalysts have made a strong impact in CO₂ hydrogenation and electroreduction and the role of molecular iron catalysts with functional ligands has recently been comprehensively reviewed.⁴⁷⁰ For hydrogenation to formic acid, the low formate hydricity (44 kcal·mol⁻¹ in MeCN) requires a catalyst with strong tendency for hydride transfer.⁶⁸ The *trans*-dihydride configuration which is stabilized by the pincer framework for iron complexes and weakens the Fe-H bonds should therefore be an ideal platform. Accordingly, Langer et al. reported in 2011 the hydrogenation of sodium

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<p>P = P<i>t</i>Bu₂ Fe-1e</p> <p>0.1 mol%</p> <p>3.29 atm CO₂, 6.57 atm H₂ 80 °C, TON = 788 TOF = 156 h⁻¹</p> <p><i>Milstein 2011</i>^[241]</p>	<p>P = PCy₂ CyFe-15a</p> <p>0.00126 mol%</p> <p>68 atm CO₂/H₂ (1:1) 80 °C, TON = 8910 TOF = 371 h⁻¹</p> <p><i>Hazari and Bernskoetter 2015</i>^[475]</p>	<p>P = PCy₂ CyFe-15Me</p> <p>0.00126 mol%</p> <p>68 atm CO₂/H₂ (1:1) 80 °C, TON = 58990 TOF = 2458 h⁻¹</p> <p><i>Hazari and Bernskoetter 2015</i>^[475]</p>	<p>P = P<i>t</i>Pr₂ Fe-22a</p> <p>0.08 mol%</p> <p>79 atm CO₂/H₂ (1:1) 80 °C, TON = 1220 TOF = 58 h⁻¹</p> <p><i>Kirchner and Gonsalvi 2016</i>^[473]</p>	<p>P = P<i>t</i>Pr₂ Fe-22Me</p> <p>0.005 mol%</p> <p>8.4 atm CO₂/H₂ (1:1) 80 °C, TON = 10275 TOF = 489 h⁻¹</p> <p><i>Kirchner and Gonsalvi 2016</i>^[473]</p>	<p>P = P<i>t</i>Bu₂ Fe-32a</p> <p>0.1 mol%</p> <p>3.3 atm CO₂, 6.2 atm H₂ 55 °C, TON = 388 TOF = 24 h⁻¹</p> <p><i>Milstein 2015</i>^[472]</p>	<p>P = P<i>t</i>Pr₂</p> <p>0.3 μmol</p> <p>34 atm CO₂/H₂ (1:1) 45 °C, TON = 450 TOF up to 28 h⁻¹</p> <p><i>Bernskoetter 2018</i>^[478]</p>
<p>P = P<i>t</i>Pr₂ Mn-22b</p> <p>1:50000 cat./DBU</p> <p>79 atm CO₂/H₂ (1:1) 100 °C, TON = 31600 TOF = 1317 h⁻¹</p> <p><i>Kirchner and Gonsalvi 2017</i>^[474]</p>	<p>P = P<i>t</i>Pr₂ Mn-22Me</p> <p>1:10000 cat./DBU</p> <p>79 atm CO₂/H₂ (1:1) 80 °C, TON = 1330 TOF = 55 h⁻¹</p> <p><i>Kirchner and Gonsalvi 2017</i>^[474]</p>	<p>P = P<i>t</i>Pr₂ iPrFe-15a</p> <p>0.02 mol%</p> <p>68 atm CO₂/H₂ (1:1) 120 °C, TON = 1930 TOF = 483 h⁻¹</p> <p><i>Bernskoetter 2018</i>^[476] N-formylation of amines</p>	<p>P = P<i>t</i>Pr₂ iPrFe-15Me</p> <p>0.02 mol%</p> <p>68 atm CO₂/H₂ (1:1) 120 °C, TON = 2440 TOF = 610 h⁻¹</p> <p><i>Bernskoetter 2018</i>^[476] N-formylation of amines</p>	<p>P = P<i>t</i>Pr₂ Co-28</p> <p>5 mol%</p> <p>30 atm CO₂/H₂ (1:1) 150 °C</p> <p><i>Milstein 2017</i>^[479] N-formylation of amines</p>	<p>P = P<i>t</i>Pr₂ iPrMn-15a</p> <p>2 mol%</p> <p>59 atm CO₂/H₂ (1:1)</p> <p><i>Prakash 2017</i>^[480] sequential hydrogenation</p>	<p>P = P<i>t</i>Pr₂ P = PCy₂</p> <p>0.3 μmol</p> <p>34 atm CO₂/H₂ (1:1) 45 °C, TON up to 29000 TOF up to 1706 h⁻¹</p> <p><i>Bernskoetter 2016/2018</i>^[477, 478]</p>

Figure 37. Summary of CO₂ hydrogenation catalysts based on PNP pincer ligands.

bicarbonate and CO₂ to formate using the pincer complex (^{*t*}BuPNP*P*)Fe(H)₂CO (**Fe-1e**) as catalyst (Scheme 50).²⁴¹ Relatively mild reaction conditions (80 °C, 8–10 atm H₂/CO₂) were leading to turnover numbers and frequencies (up to 156 h⁻¹) that could for the first time compete with molecular noble metal catalysts.⁴⁷¹

Scheme 57. Hydrogenation of sodium bicarbonate and CO₂ catalyzed by **Fe-32a** and proposed mechanism (P = P*t*Bu₂).⁴⁷²

A mechanism was proposed based on stoichiometric control experiments (Scheme 56) with CO₂ inserting into the metal hydride bond in the catalytically active dihydride species **Fe-1e**. After hydrolysis of the formate intermediate **Fe-1g**, H₂-

heterolysis closes the catalytic cycle. The role of MLC via ligand de-/aromatization for hydrogen activation remained unresolved.

The iron PNP pincer complex **Fe-32a** with an unusual pyrazine based backbone was also examined in CO₂ hydrogenation (Scheme 57).⁴⁷² Bicarbonate and CO₂ hydrogenation exhibit lower TON compared with **Fe-1e** under otherwise identical conditions.

Table 5. Sodium bicarbonate and CO₂ hydrogenation with iron PN*P*₃P pincer catalysts **Fe-22a** and **Fe-22Me**.⁴⁷³

Fe-22a R = H
Fe-22Me R = Me

precatal. (mol%)	<i>p</i> [atm]	<i>t</i> [h]	additive	solvent	yield [%]	TON
Fe-22a (0.08 mol%)	79 (CO ₂ / H ₂ 1:1)	21	NaOH (10 eq.)	H ₂ O/THF	98	1220
Fe-22Me (0.005 mol%)	8.4 (CO ₂ / H ₂ 1:1)	21	DBU (6.25 eq.)	EtOH	21	10275
Fe-22a (0.05 mol%)	89 (H ₂ / NaHCO ₃)	24	---	H ₂ O/THF	98	1964
Fe-22a (0.005 mol%)	89 (H ₂ / NaHCO ₃)	24	---	H ₂ O/THF	23	4560
Fe-22Me (0.05 mol%)	89 (H ₂ / NaHCO ₃)	24	---	H ₂ O/THF	52	1034

Stoichiometric control reactions gave rise to a proposed mechanism (Scheme 57). Interestingly, the deprotonation of precatalyst **Fe-32a** leads to polymerization of the dearomatized product via the bridging pyrazine. Deaggregation of the coordination polymer was considered to proceed either by direct H₂ heterolysis or reversible CO₂ 1,3-addition followed

by hydrogenolysis. From the *trans*-dihydride product, an analogous mechanism was proposed as for parent **Fe-1e**.

Table 6. CO₂ hydrogenation with manganese catalysts **Mn-22b** and **Mn-22Me**.⁴⁷⁴

$\text{CO}_2 + \text{H}_2$
(79 atm 1:1)

$\xrightarrow[\text{DBU, additives}]{\text{catalyst}}$

$[\text{DBUH}][\text{HCOO}]$

R = H **Mn-22b**
R = Me **Mn-22Me**

catalyst	cat./DBU ratio	solvent	T [°C]	additive	yield [%]	TON
Mn-22b	1 : 50000	THF/H ₂ O	80	-	16	9100
Mn-22Me	1 : 10000	EtOH	80	-	13	1330
Mn-22Me	1 : 50000	THF/H ₂ O	100	1 mmol LiOTf	63	31600

Kirchner, Gonsalvi and coworkers used the **PN₃P** pincer ligated iron complex **Fe-22a** for sodium bicarbonate hydrogenation with high turnover number (up to 4560) and low catalyst loading (0.005 mol%) at high hydrogen pressure (90 bar) and 80 °C (Table 5).⁴⁷³ The backbone *N*-methylated catalyst **Fe-22Me** leads to lower yield compared with parent **Fe-22a**. CO₂ hydrogenation in H₂O/THF with precatalyst **Fe-22a** (0.08 mol%) gave a turnover number of 1220. Under optimized conditions, with the backbone *N*-methylated catalyst **Fe-22Me** high TON up to 10275 could be obtained. Computational examinations for this catalyst support a dihydride/formate cycle.

Table 7. Comparison of iron diphosphinoamine pincer catalysts in the CO₂ hydrogenation.⁴⁷⁵

CO_2

$\xrightarrow[\text{THF, 80 °C, 24 h}]{\text{Fe-precatalyst, additive}}$

$\text{HCOO}^- \text{Na}^+ / [\text{DBUH}]^+$
+ H₂O

precatalyst (mol%)	p [atm]	additive	yield [%]	TON
CyFe-15a (0.00126 mol%)	68 (CO ₂ / H ₂ 1:1)	DBU (79600 eq.) LiOTf (10613 eq.)	11	8910
CyFe-15Me (0.00126 mol%)	68 (CO ₂ / H ₂ 1:1)	DBU (79600 eq.) LiOTf (15920 eq.)	74	58990

P = PCy₂
CyFe-15a

P = PCy₂
CyFe-15Me

Manganese(I) complexes with the same **PN₃P** ligands were also used for CO₂ hydrogenation. Under optimized conditions, the monohydride dicarbonyl complex **Mn-22b** exhibits TON that are almost an order of magnitude higher than with **Mn-22Me** (Table 6).⁴⁷⁴ NMR experiments revealed the formation of a formate complex with CO₂, which is also an active catalyst. Similar barriers for H₂ activation pathways with and without MLC were obtained computationally. The yield could be further enhanced by addition of Lewis acids like LiOTf (Table 6). This effect was first reported and rationalized by Hazari and Schneider for the reverse formic acid decomposition and CO₂ hydrogenation with iron pincer catalysts, which are discussed in Section 4.2 and 3.6.2, respectively.^{181,475}

3.6.2. Diphosphinoamine Pincer Catalysts Particularly active catalysts could be obtained with diphosphinoamine pincer catalysts. Hazari, Bernskoetter and coworkers reported the use of complex **CyFe-15a** for CO₂ hydrogenation with high turnover numbers in the presence of DBU as a base and LiOTf (Table 7).⁴⁷⁵ The role of the Lewis acid co-catalyst was assumed to accelerated release of formate. The formate ligand that arises from CO₂ insertion is in fact overstabilized by hydrogen bonding with the pincer secondary amine. Accordingly, the backbone *N*-methylated complex **CyFe-15Me** showed significantly increased activity with extraordinary turnover numbers (up to ca. 60000) emphasizing that the MLC pathway is not advantageous.

The CO-ligand of the catalyst was later exchanged with isonitriles, enabling steric and electronic tunability of the catalyst.¹⁹² However, the isonitrile ligated complexes exhibited turnover numbers that are about an order of magnitude lower compared with the *iso*-propyl substituted amide complex **iPrFe-15a**.

Scheme 58. *N*-Formylation of morpholine with CO₂ as carbon source catalyzed by **iPrFe-15a** and **iPrFe-15Me**.⁴⁷⁶

In the presence of amines, this catalyst can be used for *N*-formylation with CO₂ as C₁ source (Scheme 58).⁴⁷⁶ Selective morpholine *N*-formylation at high pressures and low catalyst loadings is observed. The backbone *N*-methylated borohydride complex **iPrFe-15Me** gave the best turnover numbers up to 2440.

The Bernskoetter group also reported the hydrogenation of CO₂ with analogous aminopincer cobalt precatalysts.^{477,478} As in the iron case, the *N*-methylated pincer ligands gave higher activities than the secondary amine ligands. Furthermore, the authors propose a mechanism that includes pincer hemilability of the *N*-methylated derivative.

A related cobalt pincer catalyst was used by Milstein and coworkers for the selective amine *N*-formylation with CO₂/H₂ (Scheme 59).⁴⁷⁹ In the presence of a hydride source and base the cobalt(II) complex **Co-28** catalyzed the *N*-formylation of 14 amines into the respective formamides in good to quantitative yields. The borohydride reagent reduces the precatalyst to a tetrahedral cobalt(I) complex, which exhibits catalytic activity comparable to **Co-28**. Furthermore, MLC-assisted H₂ heterolysis by a T-shape cobalt(I) amido complex was proposed, followed by CO₂ insertion, aminolysis and off-cycle formamide product formation (Scheme

59). The electronic structure of the unusual cobalt(I) intermediates remains unresolved.

Scheme 59. *N*-Formylation of amines catalyzed by cobalt(II) precatalyst **Co-28** (A) and proposed catalytic cycle (B).⁴⁷⁹

Scheme 60. Stepwise CO₂ hydrogenation to methanol via formamide with precatalyst *i*PrMn-15a (A) and proposed mechanism (B).⁴⁸⁰

Prakash and coworkers reported an example for the sequential hydrogenation of CO₂ all the way to the 6e⁻ reduction product methanol catalyzed by the manganese(I) precatalyst *i*PrMn-15a (Scheme 60).⁴⁸⁰ The overall reaction is mediated by amine, which undergoes facile, catalytic *N*-formylation in the first step in the presence of *i*PrMn-15a (2 – 4 mol%) and base (10 mol%). The *in situ* formed formamides can then be further reduced at high H₂ pressure (69–79 atm) to methanol in moderate to good yields. For the hydrogenation of

morpholine-4-carbaldehyde a turnover number of 36 could be obtained. Based on NMR monitoring, the authors proposed a catalytic cycle with the manganese(I) hydride amine (*i*PrMn-15c) and amide species (*i*PrMn-15d) as the key intermediates for MLC-assisted H₂ and CO₂ activation (Scheme 60).

3.7. Hydrogenation of Olefins

3.7.1. Pyridyl-Based Pincer Catalysts. As one of the first examples in the renaissance of 3d metal catalyzed hydroelementation, (PDI)Fe(N₂)₂ (**Fe-7i**) was shown to be an active catalyst in olefin hydrogenation (Scheme 61) with low catalyst loadings (0.3 mol%) at mild conditions (r.t., 1 atm H₂).^{298,481} A wide range of substrates can be hydrogenated in high yield (>98%). Terminal olefins are strongly favored over internal olefins and sterically demanding substrates. Chemoselective olefin hydrogenation is not affected by the presence of ester, tertiary amine, carbonyl, or other substituents. However, reduced yield is obtained for primary amines, although this catalyst is active in azide hydrogenation to primary amines.²⁹⁷ Higher catalyst loadings (5 mol%) are also required for some oxygen containing substrates and low conversion was obtained for a vinyl ester.^{158,298} Importantly, carbonyl groups were not hydrogenated.

Scheme 61. Olefin hydrogenation catalyzed by (PDI)Fe(N₂)₂ (**Fe-7i**) (Conversions determined by GC. or ¹H NMR spectroscopy).^{298,481}

Within the proposed inner-sphere mechanism (Scheme 62) the catalytically active species is suggested to be formed by N₂-dissociation, which opens a vacant coordination site for olefin coordination. Oxidative addition of dihydrogen furnishes a dihydride intermediate, which is followed by migratory insertion of the olefin into the metal-hydride bond. Reductive elimination of the alkane restores the catalytic active species. Importantly, both H₂-oxidative addition and alkane reductive elimination steps are proposed to be redox neutral for the iron(II) center but rather ligand centered redox

Figure 38. Summary of olefin hydrogenation catalysts based on tridentate PNP, PBP and PNN ligands.

processes, as shown for model reactions.^{146,148} In the absence of substrate, (**PDI**)Fe(N₂)₂ (**Fe-7i**) forms dihydrogen and σ -Si-H complexes under H₂ atmosphere and with silanes, respectively. Oxidative addition might therefore be furnished by olefin coordination.²⁹⁸ In comparison, the saturated, redox innocent bis(phosphino)pyridine ligand ^{iPr}PNP^{iPr}, which is a stronger donor, promotes metal centered oxidative addition.⁴⁸² However, the resulting hydrides are much more thermally labile than their PDI counterparts, preventing catalytic applications to date.

Budzelaar and co-workers shortly afterwards reported the catalytic hydrogenation of olefins using (**PDI**)Co platforms as catalyst. Activation of high-spin (^{iPr}PDI)CoCl₂ with excess Al(*i*Bu)₃ enabled 1-octene hydrogenation at 5–49 atm H₂ with high rates (10000 h⁻¹ atm⁻¹). Mono- and 1,2-disubstituted olefins are hydrogenated, while in case of 7-methyl-1,6-octadiene only the terminal C=C bond was reduced but not the trisubstituted olefin. NMR spectroscopic studies indicated that alkyl complexes (^{iPr}PDI)Co(R) form the hydride (^{iPr}PDI)CoH upon hydrogenolysis, which in turn inserts olefins into the Co–H bond.^{483,484} These observation lead to the proposed monohydride mechanism depicted in Scheme 62. However, an EPR signal assignable to a compound with ligand centered overall S = 1/2 spin-state was also observed in alkyl hydrogenolysis. The nature and relevance of this species for catalysis is not clear.⁴⁸³

Scheme 62: Proposed mechanism for (**PDI**)Fe- and (**PDI**) Co-catalyzed olefin hydrogenation.^{298,483}

(**PDI**)Co catalyzed olefin hydrogenation was computationally evaluated by Budzelaar and more recently by Hopman, resulting in closely related mechanistic models.^{351,485} Both studies support a monohydride mechanism with migratory olefin insertion and hydrogenolysis by σ -bond metathesis (Scheme 63) over a dihydride pathway as proposed for iron. The (**PDI**)CoH hydride species is best described as low-spin cobalt(II) antiferromagnetically coupled to a **PDI**⁻ radical anion.^{484,485} (**PDI**)CoR alkyl intermediates exhibit closed shell cobalt(I) character or spin triplet multiplicity – from antiferromagnetically coupled high-spin Co^{II} and (**PDI**⁻) – depending on the strength of the C–H agostic interaction.⁴⁸⁵ Higher spin-states seem irrelevant for all other steps of the

proposed catalytic cycle. It should be noted that the relative order of energetically closely spaced spin states can be highly dependent on the used functional due to varying degrees of electron exchange. The accessibility of closed-shell (PDI^0)Co^I and open-shell ($\text{PDI}^{\cdot-}$)Co^{II} states within the catalytic cycle augments the notion that ligand redox-activity might be a useful property for hydrogenation catalysis with this cobalt platform. However, Budzelaar's study proposed the same mechanism while only considering cobalt(I) closed-shell electronic configurations.⁴⁸³

Scheme 63. Computed mechanism for olefin hydrogenation with (PDI)Co as catalyst (AF-S: antiferromagnetically coupled singlet state; CS: closed-shell singlet state; AF-T: antiferromagnetically coupled triplet state).⁴⁸⁵

Zhu and co-workers introduced an iron PNN pincer catalyst **Fe-33** with tremendously enhanced catalytic activity by tethering a strongly donating phosphine arm to a bipyridine core (Scheme 64).⁴⁸⁶ The phosphino bipyridine ligand enables hydrogenation of several terminal olefins with wide chemical group tolerance under 30 atm pressure at r.t. with low loadings (0.1 mol%) of the *in situ* reduced (LiAlH_4) iron precatalyst. The highest activity was found for styrene with a TOF of more than 37 000 h⁻¹. In contrast, the internal olefin cyclohexene is only partially converted, even at elevated temperatures.

In situ NMR-studies suggested an iron dihydride as active species, which gave rise to a proposed iron(0)/iron(II) mechanism *via* olefin migratory insertion and alkane reductive elimination. A potentially redox supporting role of the bipyridyl unit is not clear. Bipyridine ligands can adapt the mono radical form as well as closed shell dianionic form.^{142,387} Neidig, Milstein and coworkers showed in a crystallographic, spectroscopic, electrochemical and computational study that the CO complex (**BPP**)Fe(CO)₂ is most accurately described as iron(0) with strong backbonding into a bipyridine π^* -orbital.⁴⁸⁷

Scheme 64: Iron catalyzed olefin hydrogenation. Yield determined by GC.⁴⁸⁶

Chirik iron **PDI** catalysts were extensively utilized in C-C coupling,^{161,165,166,287-293} which was thoroughly reviewed.^{4,15,55,70,71,125,126,488} For example, catalyst **Fe-7i** (Scheme 65) catalyzes the cycloaddition of α,ω -dienes.¹⁶⁵ Subsequent expansion of the scope enabled the cyclization of 1,6-enynes and diynes coupled to product hydrogenation giving a range of saturated and unsaturated cyclopropanes.²⁹⁰ Catalyst loadings of 5 mol% gave the products under mild conditions in generally high yields. The dienes obtained from reductive diyne cyclization are not further hydrogenated.

Scheme 65: Cyclization of 1,6 Enynes and Diynes followed by hydrogenation to substituted cyclopropanes.²⁹⁰ Yields referring to isolated substance.

A mechanism was proposed based on deuterium labeling experiments (Scheme 66). The $\text{Fe}^{\text{II}}(\text{PDI}^{2-})/\text{Fe}^{\text{III}}(\text{PDI}^{\cdot-})$ couple mediates the reductive two-electron coupling of the enyne substrate. Under H_2 , the metallacycle is opened by vinyl hydrogenolysis. C-H reductive elimination restores the reduced ferrous iron state. Turn-over limiting hydrogenation is suggested by an H/D kinetic isotope effect of 6.0 under D_2 .

Scheme 66: Proposed mechanism for iron-catalyzed reductive cyclization of 1,6-enynes.²⁹⁰

Table 8. Comparison of Fe³⁷³ and Co³⁷⁴ PDI and CNC type pincer catalysts in olefin hydrogenation (a: (^{Me}PDI)Fe(N₂)₂ forms a dimer; b: conversion determined by GC-FID and by ¹H NMR; d: 50 °C).

substrate	catalyst	time	conversion
	(ⁱ PrPDI)Fe(N ₂) ₂	24 h	65%
	(^{Me} PDI)Fe(N ₂) ₂	1 h	>95%
	(ⁱ PrCNC)Fe(N ₂) ₂	1 h	>95%
	(^{Mes} CNC)Fe(N ₂) ₂	1 h	35%
	(ⁱ PrCNC)CoMe	1 h	>95%
	(ⁱ PrPDI)Fe(N ₂) ₂	24 h	32%
	(^{Me} PDI)Fe(N ₂) ₂	24 h	15%
	(ⁱ PrCNC)Fe(N ₂) ₂	15 h	>95%
	(^{Mes} CNC)Fe(N ₂) ₂	1 h	>95%
	(ⁱ PrCNC)CoMe	5 h	>95%
	(ⁱ PrPDI)Fe(N ₂) ₂	24 h	0%
	(^{Me} PDI)Fe(N ₂) ₂	24 h	2%
	(ⁱ PrCNC)Fe(N ₂) ₂	24 h	20%
	(^{Mes} CNC)Fe(N ₂) ₂	1 h	>95%
	(ⁱ PrCNC)CoMe	120 h	>95%
	(ⁱ PrPDI)Fe(N ₂) ₂	24 h	0%
	(^{Me} PDI)Fe(N ₂) ₂	24 h	0%
	(ⁱ PrCNC)Fe(N ₂) ₂	24 h	0%
	(^{Mes} CNC)Fe(N ₂) ₂	24 h	0%
	(ⁱ PrCNC)CoMe ^b	24 h	69%

Pyridyldicarbenes were extensively examined in olefin hydrogenation. Comparison of catalytic activities of iron and cobalt PDI and CNC catalysts in alkene hydrogenation is

shown in Table 8.^{373,374} The carbene based pincer catalysts are in general superior particularly for the conversion of branched substrates, like 2-methyl-2-butene or 1-methyl-1-cyclohexene. The highly challenging substrate 2,3-dimethyl-2-butene, is only hydrogenated by the cobalt CNC catalyst.³⁷³ The excellent performance of the (CNC)Fe catalysts with redox innocent pincer ligands, raises the fundamental question if ligand-mediated single-electron redox behavior can generally be compensated by strong donor ligands that support 2-electron oxidative addition with 3d metals. This hypothesis is supported by the facile oxidative addition of silanes⁴⁸⁹ and dihydrogen on the (CNC)Fe(N₂)₂ (**Fe-18**) platform.⁴⁹⁰ Dinuclear oxidative addition has also been reported.^{147,149,150}

The structural related CCC (^{Mes}CCC = bis(mesityl-benzimidazol-2-ylidene)phenyl) cobalt complexes have been reported by Fout to be efficient catalysts in alkene⁴⁹¹ and alkyne⁴⁹² hydrogenation (Scheme 67). Remarkably, reactive polar substrates like aldehydes or alcohols could be efficiently converted. The catalyst was selective for terminal alkenes as displayed for isoprene where the geminal olefin stayed intact. On the basis of PHIP (parahydrogen induced polarization) transfer NMR spectroscopy studies, a mechanism is suggested which starts with the oxidative addition of dihydrogen. In the presence of olefin, the olefin coordinates to the metal and inserts into the metal hydride bond. Like in the example before it seems strong donating ligands undergo facile oxidative addition. This catalyst was furthermore active in alkyne hydrogenation to selectively form the trans product via cis-hydrogenation followed by an isomerization step. Similar to the former example, a cobalt(I)/(III) couple is operating.⁴⁹²

Scheme 67. Alkene Hydrogenation⁴⁹¹ and Alkyne Semihydrogenation⁴⁹² with a Cobalt CCC Pincer Complex **Co-34**. Conversions determined by ¹H NMR spectroscopy.

Chirik and co-workers established a *C_i* symmetric pincer platform for asymmetric, cobalt catalyzed hydrogenation of α -isopropylstyrenes (Scheme 68),²⁹⁶ reminiscent of Bianchini's catalyst for ethylene oligomerization.²⁷⁰ The precatalyst is obtained by methylation of the corresponding chloro compound with MeLi. Interestingly, alkylation with neosilyl lithium leads to pincer cyclometalation, which is reversible under an atmosphere of dihydrogen generating as alternative access to the active cobalt monohydride.²⁹⁹ Substrates with both electron donating and withdrawing groups as well as sterically demanding substrates were hydrogenated in high yield. Electron withdrawing substituents reduce the stereoselectivity.

Scheme 68. Hydrogenation of prochiral olefins with catalyst **S-(DippPDI^{Cy,Me})CoMe** (a: Yields are determined to isolated substance and GC, *ee*'s determined by GC.^{296,299}

This catalyst was further utilized for enantioselective hydrogenation of unactivated, cyclic alkenes like dialins, 1,1-diarylethenes and 1,2-dihydronaphthalenes (Scheme 68).²⁹⁹ These substrates are challenging for enantioselective hydrogenation due to hindered stereinduction. A total scope of 24 examples was examined with a broadly diversified choice of substrates using 5 mol% catalyst loading. Phenyl substituted indenenes were reduced almost quantitatively with excellent selectivity and chemical group tolerance. Hydrogenation of 1,2-dihydronaphthalenes also showed high yields and selectivities for the *S*-enantiomer. Reducing the catalyst loading to 0.1 mol% did not significantly affect yield or selectivity. Based on stoichiometric model reactions and deuterium labelling studies, Chirik and co-workers proposed a model for stereoinduction:²⁹⁹ Prochiral substrates approach the cobalt for stereo determining 1,2-insertion with the smaller substituent oriented towards the more bulky, *C*₁-symmetric alkyl imine arm of the pincer ligand.

Stereoselective, cobalt catalyzed olefin hydrogenation was also reported by Chen et al. using a chiral IPO ligand (Scheme 69). The bench stable, divalent cobalt(II) precursor is *in situ* activated by NaBEt₃H.³⁸⁴ A total scope of 32 1,1-diarylethenes as substrates was examined. Yields are generally high and high stereoselectivities were obtained for bulky and electron withdrawing substrates.³⁸⁴

Scheme 69. Stereoselective hydrogenation of 1,1-diarylethenes catalyzed by a cobalt IPO complex.³⁸⁴

3.7.2. Aminodiphosphine and Related Pincer Catalysts

Besides ketones (Section 3.1.), imines (Section 3.2.), *N*-heterocycles (Section 3.2.) and esters (Section 3.5.), first and foremost olefins are hydrogenated by Hanson's catalyst at mild conditions (Scheme 31). Activation of low-spin cobalt(II) precatalyst **Co-15a** with Brookhart's acid enabled the hydrogenation of a broad range of 12 terminal and 1,2-disubstituted aromatic and aliphatic olefins using 2 mol% catalyst loading at mild conditions (1 atm H₂, r.t., 24 h).¹⁹⁵ This work was extended for olefin transfer hydrogenation by Zhang and coworkers using *iso*-propanol as the hydrogen source.⁴⁹³ A substrate scope of 14 alkenes were hydrogenated with 2 mol% **Co-15a**/[H(EtO)₂]₂BAr^F₄ at 100 °C in *iso*-propanol/THF. The Hanson group also utilized the nickel(II) aminopincer hydride complex **Ni-15** as a catalyst in the hydrogenation of alkenes (Scheme 70).²⁰¹ With 10 mol% of **Ni-15**, a range of five alkenes could be hydrogenated. However, yields were significantly lower in the presence of other reducible groups like aldehydes.

Scheme 70. Olefin hydrogenation with precatalyst **Ni-15** (a: Yields determined by ¹H NMR spectroscopy).²⁰¹

The Hanson group reported several control experiments to gain information about the mechanism of Co- and Ni-catalyzed olefin hydrogenation.^{195,426} As pointed out above (Section 3.1.2.), the crystallographic characterization of the protonated cobalt(II) precursor remains ambiguous leaving the exact nature of this species unclear.¹⁹⁵ In continuation, the authors propose the formation of a cobalt(II) monohydride from hydrogenolysis of the protonated precursor, supported by observation of SiMe₄ and hydride trapping chloroform. Rapid olefin isomerization in the absence of H₂ and H/D scrambling crossover experiments further sustain the proposal of an active cobalt hydride species. Furthermore, in contrast to Co-catalyzed ketone reduction, the *N*-methylated precursors **Co-15Me** and **Ni-15Me** exhibit similar catalytic activities as the protonated congeners indicating no

involvement of MLC in alkene hydrogenation. Based on these observations, monohydride inner-sphere mechanisms for alkene hydrogenation were proposed for both the cobalt and nickel system (Scheme 71).^{201,426} In case of the cobalt system, the proposed mechanism is in agreement with a computational study.⁴⁹⁴ This work also showed a much higher barrier for hydrogenolysis of the neutral cobalt(II) alkyl complex $\text{Co}(\eta\text{Pr})(\text{iPrPNP})$ as an explanation for the necessity of the acid co-catalyst.

Scheme 71. Proposed Mechanism for the Cobalt and Nickel Pincer Catalyzed Alkene Hydrogenation ($\text{P} = \text{PCy}_2$).^{201,426}

Hydrogenation of a range of 11 olefin C-C double bonds with the amide catalyst iPrFe-15a was reported by Xu and coworkers.¹⁹⁶ Notably, under the applied conditions (5 mol% iPrFe-15a , 1 atm H_2 , r.t.) chemoselective alkene hydrogenation in presence of esters, nitriles and *N*-heterocycles is possible, which require higher temperatures and pressures with this catalyst, as discussed in Sections 3.5 and 3.2., respectively. However, α,β -unsaturated ketones are fully reduced to the saturated alcohols. Hammett-analysis of *para*-substituted styrenes showed strong rate acceleration for electron withdrawing substrates. Furthermore, stoichiometric styrene hydrogenation was observed for *in situ* generated $(\text{iPrPN}^{\text{H}}\text{P})\text{Fe}(\text{H})_2\text{CO}$, yet no conversion for the backbone methylated precursor $(\text{iPrPN}^{\text{Me}}\text{P})\text{Fe}(\text{BH}_4)\text{H}(\text{CO})$. These observations lead to the proposal of a stepwise outer-sphere mechanism for hydrogen transfer to the substrate. This pathway is analogous to ketone hydrogenation with this platform, yet rather unusual for olefin hydrogenation.

Scheme 72. Alkene hydrogenation with precatalyst iPrFe-15a (a: reduction to 4-phenylbutane-2-ol).¹⁹⁶

Peters and co-workers reported the unusual PBP cobalt(I) boryl complex **Co-6a** as a catalyst for rapid styrene hydrogenation with low catalyst loading at mild conditions (Scheme 73).⁴⁹⁵ The turnover frequency (1000 h^{-1}) compares well with Chirik's iron benchmark catalyst $(\text{iPrPDI})\text{Fe}(\text{N}_2)_2$ (1344 h^{-1}).²⁹⁸ **Co-6a** reversibly adds H_2 leading to the dihydrido hydroborate complex **Co-6b**.

Scheme 73. Styrene hydrogenation and stoichiometric H_2 activation by **Co-6a**.⁴⁹⁵

A related nickel(0) PBP borane catalyst for styrene hydrogenation was also reported.⁴⁹⁶ Subsequent detailed computational examination favors a novel *inverse MLC pathway* for H_2 heterolysis with hydride transfer to the functional *Z*-type borane pincer and protonation of the metal (Scheme 74).⁴⁹⁷

Scheme 74. Catalytic hydrogenation of olefins with PBP Ni(0) pincer complex **Ni-36a** and reversible H_2 activation.⁴⁹⁶

ALKYNE SEMIHYDROGENATION

Figure 39. Summary of alkyne semihydrogenation catalysts based on PNP, CCC and PNN pincer ligands.

3.8. Hydrogenation of Alkynes

Common protocols for semihydrogenation of alkynes to *Z*-alkenes apply Lindlar's catalyst, while the selective hydrogenation to *E*-alkenes is far less established despite significant progress in recent years.⁴⁹⁸ Milstein and coworker reported an iron dihydroacridine pincer catalyst for mild alkyne semihydrogenation with high *E*-selectivity (Scheme 75).⁴⁹⁹ With 2 mol% **Fe-37** predominantly substituted diphenylacetylenes were hydrogenated in almost quantitative yields and high *E/Z*-selectivity.

The groups of Luo and Liu utilized cobalt(II) PNP aminopinane pincer precatalysts for stereodivergent transfer hydrogenation of alkynes with ammonia borane as hydrogen source (Scheme 76).⁵⁰⁰ With 2 mol% of **tBuCo-15c** alkynes were converted to the respective *Z*-alkenes with predominantly good stereoselectivities and yields. In contrast, the PNN precatalyst **Co-31** gave alkenes with inverted stereoselectivity in overall good yields. Based on deuterium-labeling experiments the authors propose cobalt(I) hydride species as the active, *Z*-selective hydrogenation catalysts. However, in case of **Co-31**, the *Z*-alkene is subsequently isomerized by this species to the *E*-alkene product.

Scheme 75. Catalytic *E*-selective hydrogenation of alkynes with dihydroacridine-based Iron pincer complex **Fe-37**.⁴⁹⁹

A related cobalt(II) pyridyl pincer catalyst with *N*-morpholine substituted arms was recently applied in the *Z*-selective semihydrogenation of alkynes.⁵⁰¹ With aminoborane as the dihydrogen source 21 alkynes were reduced with predominantly high stereoselectivity. At higher temperatures, terminal alkenes are further hydrogenated to alkanes.

Scheme 76. Stereodivergent transfer semihydrogenation of alkynes with cobalt pincer precatalysts.⁵⁰⁰

In one recent report the use of an aromatized pyridyl pincer Mn(II) complex **Mn-1b** in the transfer semihydrogenation of alkynes with ammonia borane (60 – 70 °C, MeOH, 20 h) as the hydrogen source is described, however, the authors propose an inner-sphere hydrogenation mechanism without metal-ligand cooperativity.⁵⁰²

4. Dehydrogenation

4.1. (Acceptorless) Alcohol Dehydrogenation

4.1.1. Dialkylamino Pincer Catalysts Acceptorless alcohol dehydrogenation (AAD) is the oxidant-free elimination of H₂ from alcohols giving ketones or esters in the absence of further reagents. Besides the synthetic utility the hydrogen released from (bio)accessible alcohols can be the actual target in the context of chemical hydrogen storage.^{503–}

⁵⁰⁵ Methanol is of particular interest due to the high gravimetric hydrogen content (12.6%) and easy transportation. The first report on AAD of methanol with an iron pincer catalyst was reported by Beller and coworkers (Scheme 77).⁵⁰⁶ With loadings of aminopincer catalyst ***i*PrFe-15g** as low as 4.5 ppm aqueous phase reforming (APR) of methanol at 91.0 °C under basic conditions gave H₂ and CO₂ with a turnover number of 9834 after 46 hours. In analogy to catalytic CO₂ hydrogenation, which is discussed in Section 3, the iron amide complex ***i*PrFe-15a** is proposed as active species within an all-iron(II) mechanism. Subsequent improvement was achieved by Bielinski et al. employing the PNP formate complex [(*i*PrPN^HP)Fe(OC(O)H)H(CO)] (***i*PrFe-15h**) and Lewis acid LiBF₄ as co-catalyst, which resulted in a TON up to 51000 (Scheme 77).⁵⁰⁷

Scheme 77. Aqueous phase reforming of methanol with iron pincer catalysts ***i*PrFe-15g** and ***i*PrFe-15h**.^{506,507}

A mechanism supported by DFT analysis was proposed via 1) catalytic MeOH dehydrogenation formaldehyde, 2) hydrolysis of formaldehyde to methanediol, 3) dehydrogenation of methanediol to the iron formate complex ***i*PrFe-15h** and 4) Lewis-acid facilitated decarboxylation of ***i*PrFe-15h**.⁵⁰⁷ The mechanistic details for alcohol and formate dehydrogenation are identical with the respective forward reactions and were discussed there. Once again, MLC reactivity of this platform plays a pivotal role for H₂ elimination steps from the iron(II) dihydride amine species. In the absence of water methyl formate is obtained from dehydrogenation of a hemiacetal intermediate.

Scheme 78. AAD of 2° and 1° alcohols catalyzed by iron pincer Precatalyst ***i*PrFe-15g**.⁴²⁴

AAD of a broad range of primary and secondary alcohols to ketones (2° alcohols) and esters (2° alcohols), respectively, was reported by Hazari, Holthausen, Jones and Schneider (Scheme 78), with low loadings in ***i*PrFe-15g** or ***i*PrFe-15a** (0.1-1 mol%) under base free conditions.^{424,508} Lactones were obtained from diol substrates. High temperatures are required (refluxing toluene or THF) to drive the endothermic reaction by H₂ removal. DFT calculations for ester formation support an analogous mechanism as for methanol APR, yet with iron catalyzed formation of a hemiacetal that leads to the final ester product.

Subsequently, Hazari and coworkers utilized ***i*PrFe-15g** for the dehydrogenation of glycerol to lactic acid salts.⁵⁰⁹ In the presence of stoichiometric NaOH TON of 1050 was achieved in *N*-methyl-2-pyrrolidinone/water (1:1). The proposed mechanism is shown in Scheme 79.

Scheme 79. AAD of glycerol to sodium lactide with precatalyst ***i*PrFe-15g** (A) and proposed mechanism (B) (P = P*i*Pr₂).⁵⁰⁹

The use of glycerol AAD as a sustainable hydrogen source allowed for acetophenone transfer hydrogenation to 1-phenylethanol under basic conditions.⁵⁰⁹

ACCEPTORLESS ALCOHOL DEHYDROGENATION AND DEHYDROGENATIVE COUPLING OF (AMINO)ALCOHOLS

Figure 40. Summary of acceptorless alcohol dehydrogenation catalysts based on PNP dialkylamino pincer ligands.

Table 9. Dehydrogenation of diols to lactones with precatalyst ***i*PrFe-15g** (a: Yield determined by ¹H NMR spectroscopy).^{424,510}

diol	cat. loading	solvent	additive	temp. [°C]	time [h]	yield [%]
	0.5 mol%	<i>t</i> -amyl alcohol	K ₂ CO ₃ (10 mol%)	150	5	92
	1 mol%	toluene	-	120	8	96
	0.5 mol%	<i>t</i> -amyl alcohol	K ₂ CO ₃ (10 mol%)	150	5	82
	1 mol%	<i>t</i> -amyl alcohol	K ₂ CO ₃ (10 mol%)	150	5	55 ^a
	1 mol%	toluene	-	120	24	59

In continuation of the work of Jones and Schneider,⁴²⁴ Beller and co-workers reported the synthesis of several lactones by AAD of diols with borohydride complex ***i*PrFe-15g** (0.5-1 mol%) as catalyst in moderate to excellent yields (Table 9).⁵¹⁰ A three-step pathway with two catalytic dehydrogenation steps connected by intramolecular lactol cyclization was proposed (Scheme 80). Both catalytic AAD reactions were suggested to follow all-iron(II) amide/amine hydride cycles as previously proposed.⁴²⁴

Scheme 80. Proposed mechanism for dehydrogenative lactonization of diols ($P = P/Pr_2$).^{424,510}

Beller and coworkers introduced the manganese dicarbonyl amine precatalyst ***i*PrMn-15a** to methanol APR (Scheme 81).⁵¹¹ Under basic aqueous conditions a turnover number of 54 was obtained after 5 hours. Interestingly, the cyclohexyl substituted derivative **CyMn-15a** was inactive. Slightly higher TON were achieved with the tricarbonyl precursor **fac-EtMn-15b** (TON_{5h} = 65) and a mixture of MnBr(CO)₅ and ***i*PrPN^HP** (10 equiv.), respectively (TON_{5h} = 68). ***i*PrMn-15a** exhibited remarkable long-term stability (> 1 month; TON > 20000) in presence of excess of ***i*PrPN^HP**. Based on stoichiometric experiments the authors proposed *in situ* formation of five-coordinate amide complex ***R*Mn-15d** as active species that adds methanol and eliminates formaldehyde via a MLC pathway. Subsequent H₂ loss from the hydride product ***R*Mn-15c** was shown computationally for a related system.⁴⁴⁴

Scheme 81. APR of methanol with (***R*PN^HP**)Mn catalysts.⁵¹¹

In a related study, Gauvin and co-workers directly utilized the five-coordinate amide complex ***i*PrMn-15d** in AAD for the synthesis of 18 benzylic and aliphatic esters in moderate to excellent yields (Scheme 82).¹⁸⁴ Yields strongly depend on substrate sterics. No reaction was observed for neo-pentyl alcohol.

Reversible addition of the benzylic alcohol to the catalyst was spectroscopically observed. The alkoxide product forms the respective monohydride complex ***i*PrMn-15c** (and ester) upon heating. Computational treatment of the dehydrogenation pathway gave an analogous mechanistic picture as for the iron catalyst ***i*PrFe-15a**,⁴²⁴ with an all-manganese(I) amide/amine hydride MLC cycle, as previously proposed by

Beller for this system.⁵¹¹ Accordingly, the *N*-methylated hydride complex (***i*PrPN^{Me}P**)MnH(CO)₂ exhibits poor catalytic performance. As in the iron case, alcohol assisted H₂-elimination from the hydride amine state was computed as turnover limiting barrier.

Scheme 82. Dehydrogenative coupling of alcohols to esters catalyzed by ***i*PrMn-15d** (a: Yields determined by ¹H NMR spectroscopy; b: TON = 340 with 0.1 mol% ***i*PrMn-15d**).¹⁸⁴

Gauvin and coworkers further screened several ***R*PN^HP**-based (*R* = *i*Pr, Cy) iron and manganese precursors as catalysts for AAD of 1-butanol (Scheme 83) and some primary fatty alcohols to the respective carboxylic acids.⁵¹² The selectivity towards carboxylates is maintained by strongly basic aqueous conditions. Using the same reaction conditions (2 mol% cat. @ 120 °C in toluene), the five-coordinate amide complex ***i*PrMn-15d** and the borohydride (***i*PrP-N^HP**)Mn(BH₄)(CO)₂ (**Mn-15f**) exhibited similar performance and proved superior to iron catalysts presumably due to higher robustness under basic conditions.

Scheme 83. AAD of 1-butanol to butyric acid catalyzed by manganese catalysts ***i*PrMn-15d** and **Mn-15f**.⁵¹²

4.1.2. Pyridyl-Based and related Pincer Catalysts Sortais utilized the **PN₃P** ligated manganese tricarbonyl complex **Mn-22a** for AAD of 2° alcohols to ketones.⁴¹⁹ Acetophenone was obtained in 84% yield after 110 °C in toluene for 22 h. The catalyst loading (5 mol%) was considerably higher compared with the protocol for catalyst ***i*PrFe-15g** (0.1 mol%, Table 9).

Goswami and coworkers examined aerobic alcohol oxidation using the bisazophenylpyridine pincer catalysts

(**PDaz**)NiCl₂(H₂O) and (**PDaz**)ZnCl₂ (Scheme 84).¹⁷⁵ Stoichiometric amounts of KOtBu and excess zinc dust are required. Predominantly aryl-substituted primary and secondary alcohols are oxidized with low catalyst loadings (0.1-0.5 mol%) at mild conditions (1 atm O₂, r.t.) in yields between 65-96% within 2-4 h for the nickel catalyst. Zinc catalyzed oxidation required higher catalyst loadings (5 mol%) elevated temperatures and longer reaction times.^{174,175} The nickel platform was also used for oxidative condensation of aromatic alcohols and hydrazine to phthalazine.⁵¹³

Scheme 84. Aerobic oxidation of primary and secondary alcohols catalyzed by (**PDaz**)NiCl₂(H₂O) (**Ni-19**) and (**PDaz**)ZnCl₂ (**Zn-19**) (a: Yields determined by GC-MS).^{174,175}

Based on stoichiometric control experiments and DFT studies, a mechanism for aerobic alcohol oxidation was proposed (Scheme 85). Key point of the cycle is that all hydrogen transfer steps are purely ligand based within an all-nickel(II) mechanism. Initial ligand centered 1-electron reduction is supported by *in situ* EPR spectroscopy. A large H/D kinetic isotope effect was rationalized with a tunneling contribution for turn-over limiting C–H hydrogen atom transfer (HAT) from the substrate to a pincer azo-group. After proton transfer from another substrate molecule, the cycle is closed by aerobic pincer re-oxidation. H₂O₂ was detected with an iodometric assay and a hydrazo intermediate could be crystallographically characterized. Ligand centered HAT and formation of H₂O₂ resemble the enzyme galactose oxidase.⁵¹⁴ A similar mechanism was postulated for the zinc mediated dehydrogenation.^{174,175} There, a bishydrazo species could be crystallographically characterized.

Scheme 85. Proposed mechanism for nickel mediated aerobic alcohol oxidation (HAT: hydrogen atom transfer; RLS: rate limiting step).¹⁷⁵

In analogy, a ferrous phenylazophenanthroline catalyst was utilized for aerobic oxidation of primary and secondary benzylic alcohols (Scheme 86).³⁹⁷ Catalyst activation by reduction with KOtBu was confirmed by EPR spectroscopy which is also known for free phenanthroline.⁵¹⁵ With catalyst loadings of 3.0 mol% in toluene @ 75 °C good to moderate isolated yields were obtained. Electron withdrawing 4-nitrophenyl and pyridyl substituents significantly lower the yield.

Scheme 86. Aerobic oxidation of benzylic alcohols catalyzed by (**PhenAz**)FeCl₂ (isolated yields).³⁹⁷

Addition of a radical trap (TEMPO) drastically decelerated conversion in agreement with a radical mechanism. Based on kinetic and spectroscopic data, a mechanism was

proposed for the alcohol $2e^-/2H^+$ oxidation reaction via step-wise HAT from the substrate to the azo unit and subsequently to O_2 in analogy to Goswami's nickel catalyst. As a distinguishing feature, the iron catalyst was suggested to undergo one-electron iron(II)/iron(I) redox steps and one-electron step, in contrast with the all-nickel(II) and ligand two-electron redox cycle. The electronic structures of the putative iron(I) intermediates were not examined and the relevance of phenantroline redox non-innocence⁵¹⁵ for catalysis needs further clarification (Scheme 87). However, the proton coupled electron transfer (PCET)^{516–518} reactivity of the azo pincer framework provides a conceptually rare approach to cooperative catalysis, which might open new pathways for challenging substrates.

Scheme 87. Proposed mechanism for (PhenAz)FeCl₂-mediated aerobic alcohol oxidation.³⁹⁷

4.2. Formic Acid Dehydrogenation

Formic acid is of interest as a molecular hydrogen storage vector due to its high hydrogen content (4.4 wt%). Furthermore, the almost thermoneutral CO_2/HCO_2H de/hydrogenation equilibrium can be easily shifted on either side with pH enabling a cyclic, overall carbon neutral storage cycle. An important challenge is the suppression of formic acid dehydration to CO, which is a fatal catalyst poison for fuel cells.

Seminal pioneering contributions to 3d metal catalyzed formic acid dehydrogenation (FAD) were made by the Beller group.^{519–521} Iron pincer catalysts were first described by Milstein and coworkers.⁵²² The dihydride (**BuPN^{Pr}P**)Fe(H)₂CO catalyzes FAD at 40 °C in the presence

of base (NEt₃) in THF with TOF around 500 h⁻¹ and high long term stability (TON > 100000). Supported by DFT computations, the authors proposed an inner-sphere mechanism without MLC via protonation of the dihydride catalyst and subsequent CO₂ extrusion for a formate intermediate. The role of the base was not clarified.

Kirchner, Gonsalvi and co-workers used related iron **PN₃P** pincer complexes for selective FAD.⁵²³ The backbone *N*-protonated (**Fe-22a**) and *N*-methylated (**Fe-22Me**) precursors were examined. Interestingly, **Fe-22Me** exhibits TON (10000) that are an order of magnitude higher than **Fe-22a**, rendering a MLC pathway less likely, yet still possible.

Scheme 88. Formic acid dehydrogenation catalyzed by **Fe-15h** (P = *PiPr*₂).¹⁸¹

In 2014 the groups of Hazari and Schneider reported a strongly improved catalyst based on the iron diphosphinoamine pincer platform (**R^{PN^HP}**)Fe (Scheme 88).¹⁸¹ (*i***Pr**/*Cy***PNP**)Fe(H)(CO) (*i***Pr**-**Fe-15a**/*Cy*-**Fe-15a**) exhibit moderate catalytic activity. Stoichiometric experiments showed formic acid 1,2-addition giving the formate complex **Fe-15h** that can be directly used as a catalyst. Importantly, the authors demonstrated dramatically increased catalytic activity upon addition of Lewis acids. With very low catalyst loadings (0.0001 mol% **Fe-15h**) and addition of 10 mol% LiBF₄, unprecedented TOF up to almost 200000 h⁻¹ and catalyst stability (TON around 10⁶) were obtained. Within a series of Lewis acids, the rate acceleration approximately correlates with carboxylate affinity. In analogy to the systems of Milstein, Kirchner and Gonsalvi, the authors proposed an all-iron(II) mechanism without MLC (Scheme 88). The irrelevance of MLC was later supported by the higher activities obtained for the *N*-methylated catalyst (*Cy*-**PN^{Me}P**)Fe(BH₄)H(CO) in reverse CO₂ hydrogenation with respect to parent *Cy*-**Fe-15a**.⁴⁷⁵ The 'Lewis acid effect' was attributed to stabilization of a κ -H bound formate intermediate (Fe–H–CO₂···LA) of the rate limiting decarboxylation step. This interpretation could later be confirmed computationally.⁵⁰⁷ In fact, this rate acceleration by Lewis acids was shown to apply to several other FAD catalysts but also reverse CO₂ hydrogenation as discussed in Section 3.6.³³

FORMIC ACID DEHYDROGENATION

$\text{HCOOH} \xrightarrow{-\text{H}_2} \text{CO}_2$				
P = PtBu ₂ Fe-1e	P = P/Pr ₂ Fe-15h	P = P/Pr ₂ Mn-15e	P = P/Pr ₂ Fe-22a	P = P/Pr ₂ Fe-22Me
0.001 - 0.2 mol% 40 °C	0.0001 mol% 80 °C	0.3 - 1.3 mol% 65 °C	0.1 mol% 60 °C	0.01 mol% 60 °C
TON up to 100000 TOF = 417 h ⁻¹	TON up to 983642 TOF up to 196728 h ⁻¹	TON up to 190 TOF up to 14 h ⁻¹	TON up to 1000 TOF up to 716 h ⁻¹	TON up to 10000 TOF up to 2635 h ⁻¹
Milstein 2013 ^[522]	Hazari and Schneider 2014 ^[181]	Boncella 2016 ^[183]	Kirchner and Gonsalvi 2016 ^[523]	Kirchner and Gonsalvi 2016 ^[523]

Figure 41. Summary of Formic Acid Hydrogenation Catalysts Based on PNP Pincer Ligands.

Boncella and coworkers reported FAD with an analogous manganese catalyst.¹⁸³ With formate pincer complex (*i*^{Pr}P-N^HP)Mn(O₂CH)H(CO) (**Mn-15e**) TON up to 190 were obtained with catalyst loadings of 0.3-1.3 mol%.

4.3. Dehydrogenation of Nitrogen-Containing Substrates

4.3.1. Amineboranes Ammonia borane (H₃NBH₃, AB) also qualifies as candidate for chemical hydrogen storage due to the high gravimetric hydrogen density.^{524,525} Furthermore, it can be used as precursor to polymers and materials (e.g. polyaminoboranes, polyborazines, boron nitride) that represent inorganic analogues of polyhydrocarbons and carbonaceous materials.⁵²⁶ While thermal AB is generally possible, catalytic AB dehydrocoupling enables selectivity control.

Scheme 89. Catalytic dehydrogenation of ammonia borane catalyzed by *i*^{Pr}Fe-15a (P = P/Pr₂).⁵²⁷

Holthausen, Schneider and co-workers demonstrated the catalytic dehydrogenation of AB to polyaminoborane and 1 equiv. H₂ with low loadings (0.2 mol%) of the iron amido PNP pincer complex *i*^{Pr}Fe-15a (Scheme 89).⁵²⁷ Supported

by computational treatment, the authors propose an all-iron(II) MLC cycle with H₂ 1,2-addition to the catalyst by H⁺/H⁻ transfer from the N- and B-termini of the substrate, respectively, in analogy to an earlier report on a related ruthenium catalyst.¹⁸⁷

¹¹B NMR spectroscopy indicated the formation of diamino-borane HB(NH₂)₂ as a result of free aminoborane dimutation, which also releases BH₃ as a byproduct. Accordingly, the borohydride complex *i*^{Pr}Fe-15g was spectroscopically observed, which exhibits considerably lower catalytic activity than parent *i*^{Pr}Fe-15a. This observation led to a threefold improvement of the TON for this and the previously reported ruthenium catalyst upon trapping free BH₃ by addition of NEtMe₂.

The group of Beweries later reported the dehydrogenation of methylamine borane with the less active borohydride complex *i*^{Pr}Fe-15g giving high molecular weight linear polyaminoborane at room temperature.⁵²⁸ Interestingly, off-metal polymerization of highly reactive dehydrogenation product aminoborane (H₂NBH₂) was proposed despite evidence for a polymer chain growth mechanism.

In a mechanistic study, Guan and coworkers evaluated the iron POCOP pincer complex **Fe-38** for catalytic AB dehydrogenation.⁵²⁹ An unusually high degree of H₂ release (2.3-2.5 equiv. per AB) was obtained.

The authors proposed an all-iron(II) catalytic cycle (Scheme 90) involving an unusual MLC mechanism of the aryl pincer ligand. As the key step protonolysis of the aryl group by the AB N-terminus was proposed leading to release of free aminoborane. Subsequent H₂ elimination from a dihydride intermediate with a bidentate arene ligand restores the iron *ipso*-arene bond.

DEHYDROGENATION OF N-CONTAINING SUBSTRATES

Figure 42. Summary of Dehydrogenation Catalysts for *N*-Containing Substrates Based on PNP and POCOP Pincer Ligands.

Scheme 90. Proposed catalytic cycle for AB dehydrogenation catalyzed by **Fe-38** ($\text{P} = \text{P}/\text{Pr}_2$).⁵²⁹

4.3.2. *N*-Heterocycles Jones and coworkers reported the dehydrogenation of several *N*-heterocycles in moderate to excellent yields utilizing the borohydride complex ***i*PrFe-15g** as catalyst (Scheme 91).¹⁸⁰ A MLC catalytic cycle was proposed with *in situ* formed dihydride (***i*PrPN^HP**)Fe(H)₂CO and amido ***i*PrFe-15a** as active species. No semidehydrogenated intermediate was observed.

Scheme 91. Dehydrogenation of *N*-heterocycles with precatalyst complex ***i*PrFe-15g**.¹⁸⁰

Subsequently, Hanson's catalyst (**Co-15a**/[H(OEt)₂]₂BARF₄; see Section 3.1.2) was used for the dehydrogenation of *N*-heterocycles (Scheme 92).⁴⁴⁷ With 10 mol% catalyst loading five nitrogen containing heterocycles were dehydrogenated in predominantly excellent yields. Only substrates with annulated phenylene rings could be oxidized. Interestingly, the *N*-methylated cobalt complex is inactive in dehydrogenation but catalyzes the reverse hydrogenation reaction suggesting different mechanisms for forward and reverse direction.

Scheme 92. Dehydrogenation of *N*-Heterocycles with Hanson's catalyst (**Co-15b**).⁴⁴⁷

4.3.3. Dehydrogenative C-N Coupling The first dehydrogenative synthesis of lactams catalyzed by iron pincer complexes was reported by Beller and coworkers (Scheme 93).⁵¹⁰ Precatalyst complex ***i*PrFe-15g** was used to transform nine aminoalcohols into the respective lactams. Despite higher catalyst loading yields are generally lower than for lactone synthesis. Four-membered β-lactams, which

lead structures in antibiotic drugs, could not be obtained with this methodology.^{530–532} In contrast, five- to eight-membered heterocycles were obtained in good yields. With annelated phenylene groups indoles and 3,4-dihydroisoquinolines were obtained, due to competing dehydration of the hemi-aminal intermediates.

Scheme 93. Dehydrogenative coupling of aminoalcohols to lactams catalyzed by ***i*PrFe-15g** (a: ¹H NMR spectroscopic yield)⁵¹⁰

Bernskoetter and coworkers reported highly efficient intermolecular dehydrogenative coupling of alcohols and secondary amines to (form)amides using low loadings (0.1 mol%) of iron amide complex ***i*PrFe-15a**.⁵³³ A strong dependency on substrate sterics was observed, resulting in higher turnover numbers for sterically undemanding amines and alcohols (Scheme 94).

Scheme 94. Coupling of methanol and 1,2,3,4-tetrahydroisoquinoline catalyzed by ***i*PrFe-15a**.⁵³³

Milstein and coworkers reported dehydrogenative *N*-formylation of amines using methanol as C₁ building block catalyzed by the PNP manganese pincer complex **Mn-28a** (Scheme 95).⁵³⁴ This process represents the reverse reaction of the last step within CO₂ to methanol hydrogenation via formamide intermediates established by Prakash and coworkers, as discussed in Section 3.6.⁴⁸⁰ A range of 14 aromatic and aliphatic amines could be *N*-formylated in moderate to good yields at 110 °C in methanolic solution.

Scheme 95. Dehydrogenation reactions catalyzed by **Mn-28a**.^{534–536}

Stoichiometric experiments suggest an unusual variant of MLC with this ligand. The manganese dicarbonyl amide complex **Mn-28c** was isolated from dehydrohalogenation of bromide **Mn-28b** (Scheme 96) and adds methanol by 1,2-addition across the Mn–N bond. These observations suggest the typical all-Mn(I) amide / hydride amine cycle for alcohol dehydrogenation. However, the amide complex **Mn-28c** turned out to be thermally unstable and isomerizes under catalytic conditions (110 °C) to the benzylic C–H metalated amine tautomer **Mn-28d** (Scheme 96). In fact, H₂ elimination from the hydride amine catalyst **Mn-28a** directly leads to **Mn-28d**, which was computed to be more stable than the amide isomer by 9.7 kcal·mol^{–1}. Importantly, **Mn-28d** is catalytically active and therefore represents the catalyst resting state. Formation of the final product is maintained by subsequent dehydrogenation of the hemiaminal intermediate that results from addition of amine to formaldehyde.

DEHYDROGENATIVE C-N COUPLING AND AMINOMETHYLATION

Figure 43. Summary of catalysts for the dehydrogenative C-N coupling and aminomethylation based on PNP and PNN pincer ligands.

Milstein subsequently established cascade-type alcohol functionalization that is based on initial manganese

catalyzed dehydrogenation. As a first example, catalyst **Mn-28a** was further utilized in the deoxygenation of primary

alcohols (Scheme 95).⁵³⁵ With hydrazine as reductant, a range of 15 primary alcohols transformed to the respective alkanes in good yields. Other reducible or coordinating functional groups led to significantly lower yields, e.g. for the allylic alcohol (*E*)-3-phenylprop-2-en-1-ol giving 53 % 1-phenylpropane. The authors propose that the product is formed by Wolff-Kishner reaction of the aldehyde from manganese catalyzed alcohol dehydrogenation via an MLC mechanism. In the absence of base deoxygenation is also observed, yet with lower yields, suggesting that Mn catalyzed hydrazone N-H activation might be possible.

Scheme 96. Stoichiometric reactivity of the manganese pincer platform **Mn-28b** (P = *PiPr*₂).⁵³⁴

Dehydrogenative α -olefination of nitriles with primary alcohols as alkylidene source was subsequently reported for catalyst **Mn-28a** (Scheme 95).⁵³⁶ A range of 16 different vinyl nitriles were obtained in low to very good yields using 4 mol% **Mn-28a**. Substrate scope includes (hetero)aromatic as well as aliphatic primary alcohols and predominantly benzylic nitriles. As for nitrile deoxygenation, the authors propose cascade-type functionalization of the *in situ* formed aldehyde from primary AAD, in this case by Knoevenagel condensation with the nitrile. Besides AAD, the catalyst was ascribed an active role in nitrile activation, which are more acidic ($pK_a^{\text{dmsO}}(\text{PhCH}_2\text{CN}) = 22$)⁵³⁷ than primary alcohols (Scheme 97). It remains unclear if free or coordinated cyanophenylmethanide undergoes the C–C bond forming step.

The pyridine-based PNN pincer catalyst **Mn-29a** was used to synthesize cyclic imides via acceptorless dehydrogenative coupling of diols and amines releasing 4 equiv. H_2 (Scheme 98).⁵³⁸ With 5 mol% catalyst loading and activation with 10 mol% KH, a range of 16 cyclic imides were obtained. Benzylic amines generally give higher yields than aliphatic amines. In the absence of the amine, the respective lactones are obtained, which give imides with the amine under catalytic conditions and might therefore be intermediates. In a related study the same catalyst was used for linear amide synthesis by dehydrogenative coupling of alcohols and amines.⁵³⁹

Scheme 97. Proposed mechanism for α -olefination of nitriles catalyzed by **Mn-28a** (P = *PiPr*₂).⁵³⁶

The proposed mechanism implies stepwise, MLC-assisted, catalytic dehydrogenation to lactone and subsequent aminolysis or alternatively hemiaminal formation on the intermediate aldehyde stage. MLC is supported by the catalytic inactivity of the analogous complex with tertiary amine CH_2NEt_2 pincer arm. Furthermore, the amide derivative of **Mn-29a** is also catalytically active. Hemilability of the amine donor was discussed as being potentially useful for β -H elimination at the alkoxide intermediate.

Scheme 98. Dehydrogenative lactam synthesis from diols and amines catalyzed by **Mn-29a**.⁵³⁸

This approach has led to several protocols for the synthesis of aromatic heterocycles. Dehydrogenation of secondary 1,4-diols by the cobalt pincer precatalyst **Co-29** (5 mol%) in the presence of primary amines provides a versatile route to a range of 1,2,5-substituted pyrroles in low to excellent yields (Scheme 99).⁵⁴⁰ Catalytic amounts of a hydride source (NaBEt_3H) and base are further required. Stoichiometric reaction with NaBEt_3H produced a cobalt(I) chloride complex that exhibits similar catalytic activity.⁴⁶⁷ This cobalt platform is also an active catalyst for the synthesis of benzimidazoles by dehydrogenative coupling of aromatic diamines

and primary alcohols (Scheme 99).⁵⁴¹ Under base-free conditions a range of 18 benzimidazoles was isolated.

Scheme 99. Dehydrogenative cobalt-catalyzed coupling of diols with primary amines to form substituted pyrroles.^{540,541}

Balaraman and coworkers reported the use of a cobalt(II) SNS aminopincer precatalyst for the dehydrogenative coupling of aminoalcohols and alcohols to substituted *N*-heterocycles.⁵⁴² A broad range of 15 pyrroles, 11 pyridines and quinolines and one pyrazine was obtained in moderate to good yields.

Pyrazines and quinoxalines were synthesized by Milstein with the dehydrogenative coupling approach catalyzed by the acridine-based manganese pincer complex **Mn-37** (Scheme 100).⁵⁴³ Activation was achieved using potassium hydride at high temperatures in toluene, releasing dihydrogen and water as stoichiometric byproducts.

Scheme 100. Manganese catalyzed synthesis of pyrazines and quinoxalines via dehydrogenative coupling.⁵⁴³

Manganese catalysts based on the **PN₃P** and **PN₅P** pincer ligand system are also used for dehydrogenative multicomponent syntheses of nitrogen containing heterocycles like pyrroles, quinolines and pyrimidines. Kempe and coworkers demonstrated the formation of 2,3,5-substituted pyrroles via dehydrogenative coupling of secondary alcohols with aminoalcohols catalyzed by **PN₅P** pincer ligated complex **Mn-23** (Scheme 101).⁵⁴⁴ A broad range of 20 products and 9

further examples with a similar precatalyst could be obtained. Iron and cobalt complexes with the same type of pincer ligands showed no catalytic activity and the manganese catalyst even surpasses the yields obtained with an analogous iridium complex at milder reaction conditions. Stoichiometric reaction of **Mn-23** with KOtBu/H₂ gave the respective manganese(I) hydride, which is also catalytically active, leading to a proposed all-manganese(I) dearomatized amide / aromatized hydride cycle.

Kirchner and coworkers utilized the related aromatized **PN₃P** hydride catalyst **Mn-22b** for quinoline synthesis upon dehydrogenative coupling of 2-aminobenzyl alcohol upon secondary alcohol (Scheme 101, bottom arrow).⁵⁴⁵ Interestingly, the *N*-methylated analogon of **Mn-22b** proved inactive, suggesting the relevance of MLC. A range of 16 quinolines was synthesized with a catalyst loading of 5 mol% in the presence of KOtBu/KOH at 140 °C.

Scheme 101. Dehydrogenative multicomponent reactions to pyrroles, quinolines and pyrimidines catalyzed by manganese **PN₃P** and **PN₅P** pincer complexes.^{250,544,545}

Both manganese platforms were utilized for dehydrogenative coupling of benzamidine with primary and secondary alcohols to substituted pyrimidines (Scheme 101). With Kirchner's catalyst **Mn-22b**, addition of KOH is required,⁵⁴⁵

while Kempe's catalyst **Mn-23** operates at lower temperatures only using KOtBu as base.²⁵⁰

4.3.4. Dehydrogenative Aminomethylation Dehydrogenative aminomethylation of aromatic compounds with methanol as the C₁ building block has been reported by Kirchner and co-workers using the monohydride catalyst **Mn-22b** (Scheme 102).⁵⁴⁶ A range of 28 (hetero)aromatic products were obtained in moderate to good yields with a catalyst loading of 4 mol% and 1.3 equivalents KOtBu. In the absence of amine two aromatic cores were coupled to bisarylmethane products. With the related iron(II) hydride complex **Fe-22a**, methylation aromatics were mainly obtained (ca. 50%).

Scheme 102. Dehydrogenative aminomethylation of aromatic compounds catalyzed by manganese(I) catalyst **Mn-22b**.⁵⁴⁶

5 HYDROGEN BORROWING METHODOLOGY

The 'hydrogen borrowing' methodology is a synthetic strategy for transformations via dehydrogenation, functionalization and rehydrogenation reactions that are net redox-neutral.^{547–553} The dehydrogenation of the nucleophilic alcohol group implies an umpolung to the electrophilic carbonyl functionality thereby opening up follow-up reactivity, like condensation reactions or aldol reactivity. Typical reactions are condensations like *N*-alkylation reactions, carbonyl and alcohol α -alkylations (Scheme 103) that allow for versatile C–N and C–C bond formation with alcohols as hydrocarbon source. The hydrogen borrowing methodology is therefore an attractive approach for expanding the scope of renewable carbon sources as feedstock for value-added products.

Hanson and coworkers reported the base-free synthesis of imines by AAD with cobalt(II) catalyst (^{Cy}PNP)Co(CH₂SiMe₃)/[H(OEt)₂][BAr^F₄] (**Co-15b**) in the presence of primary amines (Scheme 103).⁵⁵⁴ This work was expanded by Zheng's group demonstrating that the addition of molecular sieves and longer reaction times lead to secondary amines in moderate to excellent yields (Scheme 103).⁵⁵⁵ Under these conditions, the immediate imine condensation products are rehydrogenated to give a redox-neutral formal condensation reaction of the amine and alcohol precursors. Secondary amines could also be obtained with Hanson's

catalyst from condensation of two amine precursors and elimination of ammonia (Scheme 103).⁵⁵⁶ Heterocoupling was achieved with primary or secondary amines and anilines to alkyl aryl amines. Diamines gave cyclic products.

Scheme 103. Hydrogen borrowing coupling reactions catalyzed by Hanson's catalyst.^{554–557}

Further hydrogen borrowing applications with this catalyst were described, such as the α -alkylation of ketones with primary alcohols (Scheme 103).⁵⁵⁷ This reaction relies on aldol condensation of the AAD product and subsequent catalytic C–C rehydrogenation of the α,β -unsaturated product (Scheme 103). In addition, a modified dehydrogenative Friedländer synthesis of quinolones was described with moderate yields that utilizes aminoalcohols and ketones, as discussed in Section 4.3.3.

Similar reactivity was reported by Kempe's group with their **PNsP** cobalt(II) precatalyst **Co-23c**. Dehydrogenative alkylation of aromatic amines with primary alcohols lead to a broad range of 33 secondary anilines and dianilines in moderate to excellent yields at low catalyst loading (2 mol%; Scheme 104).⁵⁵⁸ Related **PNsP** catalyst **Co-23b** (5 mol%) was used for alkylation of secondary alcohols with primary alcohols (Scheme 104).⁵⁵⁹ Stoichiometric experiments support the hydrogen borrowing mechanism. Catalysts **Co-23b** and **Co-23c** were further utilized for the α -alkylation of unactivated amides and esters (Scheme 104).⁵⁶⁰ A broad range of 22 *C*-alkylated amides and 12 *C*-alkylated ester were obtained in moderate to high yields. The authors showed that

Figure 44. Summary of catalysts for the *N*-alkylation of amines with alcohols and for the coupling of amines involving a hydrogen borrowing reaction sequence based on PNP pincer ligands.

the steady-state concentration of the aldol condensation intermediate should be low to avoid side reactions.

Scheme 104. Hydrogen borrowing alkylations of amines, alcohols, amides and esters using cobalt **PN₃P** catalysts.^{558–560}

Intermolecular coupling of amines and alcohols was described by Kirchner and coworkers using iron(II) and manganese(I) pincer precatalysts with divergent reactivity.⁵⁶¹ The Mn-based **PN₃P** catalysts selectively gave imines while the iron analogs resulted in the amine hydrogen borrowing products.

Scheme 105. Amine alkylation catalyzed by **PN₅P** iron catalyst **Fe-23**.⁵⁶²

In a comparative study, the Kirchner group investigated a range of different **PN^{Pr}P**, **PN₃P** and **PN₅P** iron pincer catalysts for amine alkylation (Scheme 105).⁵⁶² A vast range of aliphatic and (hetero)aromatic amines was obtained in predominantly moderate to excellent yields with the **PN₅P** catalyst **Fe-23**. A hydrogen borrowing mechanism via AAD, imine condensation and rehydrogenation with dearomatization/aromatization based MLC was proposed.

Figure 45. Summary of PNP and PNN pincer complexes catalyzing hydrogen borrowing reaction sequence incorporating transformations.

The Beller group introduced manganese pincer complexes to amine *N*-alkylation with alcohols. The diaminophosphine-based precatalyst *i*PrMn-15a (3 mol%) produced 42 different *N*-alkylated aromatic amines in presence of base in moderate to high yields (Scheme 106).⁵⁶³ Heterocyclic products generally exhibit lower yields than carbocyclic derivatives. Tertiary amines were observed as products.

Scheme 106. *N*-alkylation of aromatic amines catalyzed by *i*PrMn-15a, Mn-22a and Mn-1a.^{563–565}

Selective primary amine *N*-methylation is particularly challenging due to more demanding dehydrogenation of methanol and a high tendency for dialkylation. The *i*PrMn-15a catalyzed reaction allowed for *N*-methylation of 14 anilines. An

improved protocol gave *N*-methylation of 17 aromatic amines with precatalyst Mn-1a at milder reaction conditions tolerating several other functional groups like ketones, C-C double bonds and amides (Scheme 106).⁵⁶⁴

A range of 19 anilines were *N*-methylated with methanol as C₁ source using the manganese PN₃P pincer tricarbonyl complex Mn-22a by the group of Sortais (Scheme 106).⁵⁶⁵ The reaction requires relatively low base (0.2 equiv. KOtBu) but significantly higher catalyst loadings 5 mol%

Scheme 107. α -Alkylation of ketones with primary alcohols using manganese catalyst *i*PrMn-15a.⁵⁶⁶

The α -alkylation of ketones with primary alcohols was also carried out with the bifunctional manganese catalysts *i*PrMn-15a. With 2 mol% loading and activation by Cs₂CO₃ a broad range of 34 substrates could be α -alkylated in mainly good to excellent yields (Scheme 107).⁵⁶⁶ Besides methylketones some cyclic ketones were also reported as substrates. Phenylallyl alcohol as source for the alkyl synthon gave low yields. The authors assume a typical hydrogen borrowing mechanism via AAD, aldol condensation with the enolizable ketone and catalytic C=C rehydrogenation. However, a rather unusual MLC path for the AAD step was proposed with β -H-transfer from an alkoxide to the pincer amide ligand of a manganese(I) ate-intermediate. This reductive elimination

reaction leads to an unprecedented manganese(I/I) AAD redox mechanism to rationalize the statistical deuterium distribution in the product α - and β -positions when starting from a HOCD_2Ph isotopomer (Scheme 108). However, N–H/Mn–D scrambling on the manganese(I) hydride amine stage via a dihydrogen intermediate provides a more established, alternative path to rationalize the labeling experiments. A mechanistic study for this reaction is yet to be carried out.

Scheme 108. A: Proposed Mechanism for the α -Alkylation of ketones with primary alcohols using $^i\text{PrMn-15a}$ featuring an unprecedented manganese (I/I) AAD redox mechanism. B: Deuteration experiments using a HOCD_2Ph alcohol isotopomer ($\text{P} = \text{P}^i\text{Pr}_2$).⁵⁶⁶

The Guerbet reaction, i.e. the β -alkylation of alcohols by homocoupling and elimination of water, represents an interesting upgrading reaction of bioavailable alcohols like ethanol to long-chain alcohols. The reaction has also been reported with bifunctional 3d pincer catalysts as an extension of previously described ketone α -alkylation that requires AAD of both fragments prior to aldol condensation and rehydrogenation with half of the released H_2 (Scheme 109). Two groups independently utilized precatalyst $^i\text{PrMn-15a}$ for Guerbet condensation of ethanol to butanol.^{567,568} The protocol established by Liu and co-workers achieved turnover numbers up to 114120 over a reaction time of 168 h in neat ethanol (Scheme 109) with extremely low catalyst load (0.0001 mol%)⁵⁶⁷ The respective backbone *N*-methylated catalyst showed significantly lower catalytic activity suggesting the relevance of MLC for the AAD cycle.

Scheme 109. Liu's protocol for Guerbet-condensation of ethanol to 1-butanol catalyzed by $^i\text{PrMn-15a}$ (A) and proposed mechanism for product formation via a hydrogen borrowing sequence (B).⁵⁶⁷

Milstein recently reported the synthesis of *N*-substituted hydrazones from alcohols and hydrazine (Scheme 110).⁵⁶⁹ 3 mol% of the PNN pincer catalyst **Mn-33** were employed to obtain a range of 10 hydrazones in predominantly good yields. The dearomatized, five-coordinate Mn(I)-species could be isolated and showed catalytic activity, albeit with lower yield. Reaction with benzylic alcohol generated the respective alkoxide by O–H 1,3-addition, which formed the hydride upon heating. Based on these observations, an MLC mechanism was proposed for AAD, which is coupled to condensation with the hydrazine and only one catalytic rehydrogenation step resulting in a remarkable selectivity for the half reduced azine product (Scheme 110).

Scheme 110. Synthesis of *N*-substituted hydrazones by manganese catalyzed coupling of alcohols with hydrazine ($\text{P} = \text{P}^t\text{Bu}_2$).⁵⁶⁹

Maji and coworkers described the α -alkylation of ketones with primary alcohols using a phosphine-free NNN pincer manganese (I) catalyst (Scheme 111).⁵⁷⁰ The acidic N–H group in the backbone can serve as proton relay by 2-hydrazinopyridine de-/aromatization, in analogy to the popular PN^3P , PN_3P and PN_5P ligands, enabling cooperative E–H bond heterolysis by 1,3-addition. The active catalyst was formed *in situ* from ligand **L1** and $[\text{Mn}(\text{CO})_5\text{Br}]$ precursors in presence of KO^tBu and a catalytic cycle based on cooperative AAD was proposed. Furthermore, the dehydrogenative Friedländer synthesis of quinolines was reported (Scheme 111).

Scheme 111. Dehydrogenative α -alkylation of ketones with primary alcohols and Friedländer synthesis with a manganese NNN pincer catalyst and proposed mechanism.⁵⁷⁰

6 OUTLOOK

The field of 3d metal pincer catalysis emerged as a competitive branch in homogeneous de-/hydrogenation catalysis over the past 10 years. The success was strongly inspired by the introduction of functional pincer ligands such as metal-ligand platforms that facilitate bond activation reactions by metal-ligand cooperativity. Experimental and particularly computational studies continuously refine the initial mechanistic picture. The functional pincer ligand platforms do not universally undergo reversible de-/protonation reactions in the course of catalysis. However, the conceptual impact of MLC-assisted stoichiometric bond activation continues to stimulate the design of new ligands and exploitation of base metals that were traditionally not suitable for de-/hydrogenation catalysis. These developments are to a large extent empirically driven. Future systematic studies on thermochemical and kinetic properties, such as hydride and ligand BDFE, pK_a and hydricity values or hydrogen transfer rates, will be required to offer predictive tools for catalyst development and benchmarking data for computational support.

Another driving concept was the use of redox-active, weak-field pincer ligands that impose precious metal-like catalytic activity. The impact of these platforms in de-/hydrogenation

is not as extensive as in other fields of catalysis such as C-C coupling. However, the emergence of systems that undergo stoichiometric and catalytic ligand-based proton coupled electron transfer complements the rapidly growing toolbox of functional pincer ligands and might lead to new applications for first-row metal catalyzed transformations.

3d metal de-/hydrogenation is dominated by iron pincer catalysts. Iron still offers the highest activities enabling in some cases catalysis with loadings in the ppm range. Suitable catalyst precursors are readily synthetically accessible and were developed as a direct extension of ruthenium and osmium catalysis. However, manganese is a ‘rising star’ rapidly catching up. Cobalt precatalysts with functional pincer catalysts are particularly useful for the hydrogenation of unpolar substrates, such as olefins. Their open-shell electronic states hampers the development of a comprehensive mechanistic picture to the same extent as for iron and manganese leaving ample room for future work. The expansion of the isoelectronic iron(II) and manganese(I) series to cobalt(III) or chromium(0) will be challenging goals for catalyst design.

The current catalytic scope focuses on the transformation of polar substrates that can be activated by metal-ligand cooperative pincer platforms. In that context, several frontiers still remain, such as the hydrogenation of CO_2 beyond formate to methanol or even methane. The direct hydrogenation or carbonic acids provides another challenging task. Catalytic alkane dehydrogenation, which strongly benefitted from the application of pincer ligands, is still confined to precious metal catalysis. And certainly the catalytic reduction of dinitrogen, which is carried out industrially in massive scale with a heterogeneous iron catalyst, is waiting for an efficient catalytic solution at ambient conditions. The introduction of functional pincer ligands that facilitate proton coupled electron transfer to such challenging substrates offers strategies for the development of thermal, electrochemical and photochemical catalysts.

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ACKNOWLEDGMENT

This paper is dedicated to Prof. Dr. Dietmar Stalke on the occasion of his 60th birthday. S.Sch. acknowledges to the European Research Council (ERC Grant Agreement 646747) for funding.

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