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Homogeneous Catalysis by Cobalt and Manganese Pincer Complexes

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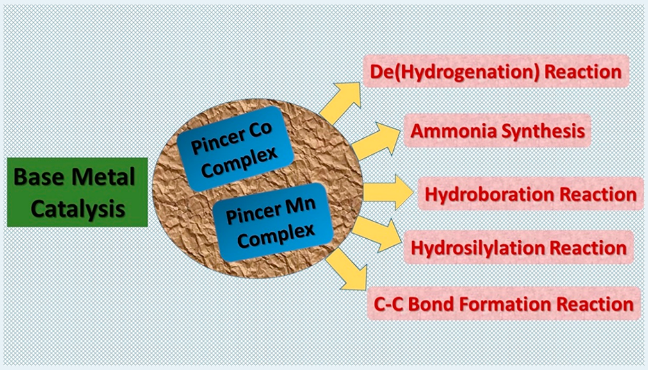
ABSTRACT: Homogeneous catalysis of organic transformations by metal complexes has been mostly based on complexes of noble metals. In recent years, tremendous progress has been made in the field of base-metal catalysis, mostly with pincer-type complexes, such as iron, cobalt, nickel, and manganese pincer systems. Particularly impressive is the explosive growth in the catalysis by Mn-based pincer complexes, the first such complexes being reported as recently as 2016. This review covers recent progress in the field of homogeneously catalyzed reactions using pincer-type complexes of cobalt and manganese. Various reactions are described, including acceptorless dehydrogenation, hydrogenation, dehydrogenative coupling, hydrogen borrowing, hydrogen transfer, H−X additions, C−C coupling, alkene polymerization and N_2 fixation, including their scope and brief mechanistic comments.



KEYWORDS: *pincer ligand, homogenous catalysis, earth-abundant metal, cobalt, manganese*

1. INTRODUCTION

Rational design and the choice of an appropriate ligand are very important for the development and fine tuning of the catalytic activities and stereoselectivities of metal complexes. The steric and electronic properties imparted by the ligand greatly influence the nature of the reactive species and thus the outcome of a homogeneously catalyzed reaction.[1]

In general, pincer-based ligands provide exceptional stability and reactivity of the metal complexes obtained toward various transformations. As a result, the chemistry of pincer-type complexes has been extensively developed in the last few decades.[2] The pincer ligand can be designed in a few steps, and its electronic and steric nature can be readily tuned. Additionally, the tridentate coordination mode forms a well-defined geometry around the metal center and provides better flexibility and capability for adapting to the requirements of the different steps of the catalytic cycle during catalysis. Moreover, pincer complexes capable of cooperation between the metal center and the pincer ligand, undergoing both bond-making and -breaking processes with incoming substrates, provide new opportunities for catalytic design.[3] Owing to these advantages, in the past few years a plethora of these ligands have been reported and their metal complexes have been explored in various transformations.[2]

Over the past decades, metal complexes, mostly based on noble metals, have been explored in a variety of chemical transformations.[4,5] However, the recent trend is the replacement of noble-metal catalysts by more economical, environmentally friendly catalysts based on earth-abundant metals. Moreover, first-row transition metals can exhibit different coordination geometries and multiple spin states that help in the manipulation of the electronic structure of the resulting complex as required during different steps of the catalysis. In addition to this, the first-row transition metals can provide more substitutional lability in comparison to that of second- and third-row transition metals. However, the tendency of first-row transition-metal complexes to react by one-electron pathways, rather than by the prevailing two-electron transformations of second- and third-row metals, can make it difficult to envisage and control catalytic reactivity. In this regard, bond activation by metal−ligand cooperation can proceed with no change in the metal oxidation state, which makes such processes more suitable for adaptation by first-row metals.[3a] Moreover, other approaches have also been employed for the first-row transition-metal catalysis to enable the two-electron processes: e.g. employment of redox-active ligands[6] and metal−metal cooperativity.[7] Hence, first-row transition metals might provide different mechanisms and different selectivities in comparison with second- and third-row transition metals. Neutral ligand systems, such as CO, phosphines, etc., may also promote catalysis with first-row metals.[8] As a result of this, in the past few years noteworthy progress has been made in the area of homogeneous earth-abundant metal catalysts in various organic transformations.

In recent years, several reviews have been published, focusing on pincer complexes based on noble metals such as

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ruthenium, iridium, palladium, and platinum.[4,5] Fewer reviews related to earth-abundant metals, such as iron,[9] cobalt,[6,10] and manganese,[11] have been published. Recently, reviews focusing on the development and application of iron pincer complexes[6] have been reported, while there have been very few reviews on well-defined cobalt and manganese pincer complexes.[7,8] This review will focus on the recent advancements in the field of homogeneous catalysis by cobalt and manganese pincer complexes.

Base-metal complexes can catalyze a range of organic transformations, including (de)hydrogenation, C−C coupling, C−H borylation, hydrosilylation, polymerization, etc. In section 2 we discuss dehydrogenation reactions catalyzed by cobalt and manganese pincer complexes. This includes acceptorless dehydrogenation of alcohols, followed by reaction with nucleophiles to yield imines, amine heterocycles, esters, and amides. Next, we discuss hydrogenation reactions using molecular hydrogen for the synthesis of alcohols, amines, alkanes, etc. We further cover catalytic reduction using hydrogen donors (transfer hydrogenation) and proceed to more intricate chemistry. We then discuss the application of cobalt and manganese pincer complexes in other useful organic transformations.

2. DEHYDROGENATION REACTIONS

Significant progress has been made during the past few decades in metal-catalyzed dehydrogenation reactions of alcohols. Alcohols are available from lignocellulose,[12] which is an abundantly available biomass. It is indigestible and is used very rarely, and therefore it is an attractive nonfossil carbon source.[13] Alcohols can be activated toward new reactivity modes by dehydrogenation, while releasing as a byproduct valuable dihydrogen. During the last two decades, several highly efficient catalytic systems have been developed for dehydrogenation processes using complexes of noble metals.[5c,d] In addition, significant progress has been made in recent years regarding dehydrogenation reactions catalyzed by complexes of earth-abundant metals.[9−11] Herein, we discuss the dehydrogenation reactions catalyzed by cobalt and manganese pincer complexes.

Dehydrogenation of a primary alcohol leads to an aldehyde that can react with an alcohol or an amine, leading to the formation of a hemiacetal or hemiaminal, respectively. These can be dehydrogenated to form the corresponding ester or amide, respectively. The main advantages associated with this process in comparison with established synthetic routes are the use of cheap starting materials (alcohols) and the generation of H_2, valuable by itself, as a byproduct.

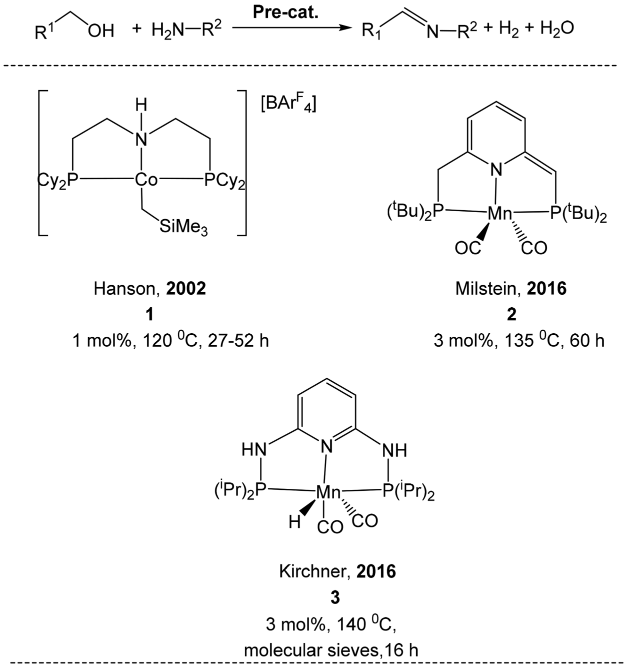
Alternatively, a borrowing hydrogen approach can also take place if the hydrogen (or metal hydride intermediates), formed in a dehydrogenation step, can be transferred to an unsaturated intermediate.

2.1. Synthesis of Imines.

The catalytic synthesis of imines by dehydrogenative coupling of alcohols with amines represents an environmentally benign methodology, which produces only H_2 and H_2O as byproducts. Mechanistically, the initially formed aldehyde generated by the metal-catalyzed alcohol dehydrogenation reacts with the amine to form a hemiaminal intermediate, which loses a molecule of water instead of taking part in another catalytic cycle. In 2010, Milstein and co-workers[14] first reported the dehydrogenative coupling of amines and alcohols to form imines, catalyzed by a PNP-ruthenium pincer complex. Following this report, several groups have developed imine synthesis with precious-metal catalysts.[15]

Zhang and Hanson reported[16] the first imine synthesis catalyzed by the PNP-pincer cobalt complex **1** (Scheme 1).

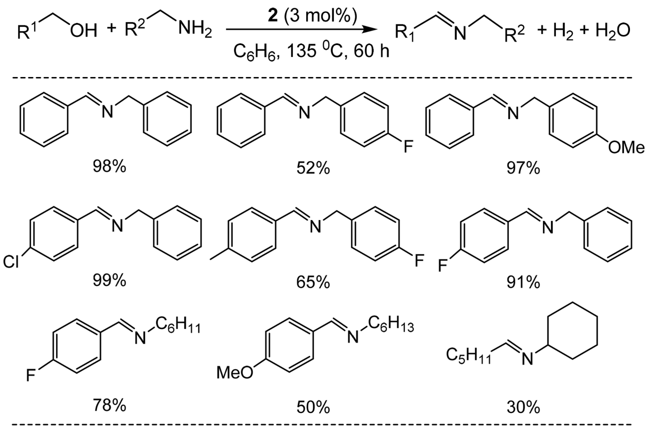
Scheme 1. Synthesis of Imines Catalyzed by Cobalt and Manganese Complexes 1−3



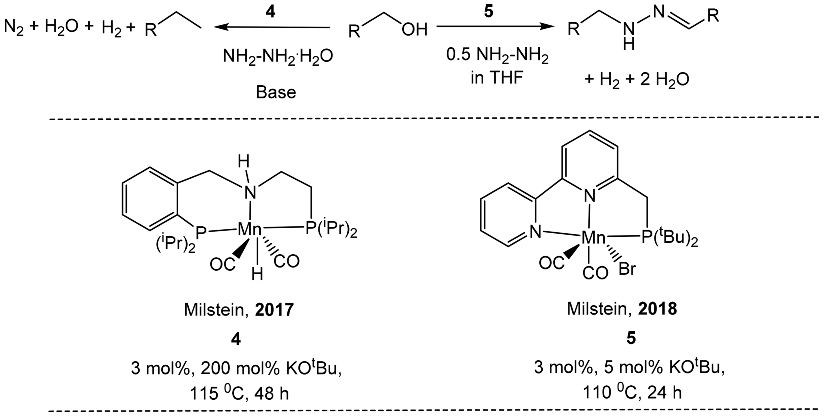
Various functional groups, including electron-donating and electron-withdrawing substituents, were tolerated under the catalytic conditions. Both aliphatic and aromatic alcohols and amines were converted to the corresponding imines in good yields (up to 99%). Interestingly, the cationic cobalt precatalyst proved to be essential for the imine formation reaction. When a neutral cobalt alkyl complex was used instead, the imine was obtained in low yield (7%) even after 24 h. A deuterium labeling experiment indicated that the imine formation reaction proceeds by an initial reversible alcohol dehydrogenation step involving a cobalt hydride intermediate.

In 2016 Milstein and co-workers[17] reported the unprecedented manganese-catalyzed acceptorless dehydrogenative coupling of alcohols and amines to yield imines. The manganese complex **2** exhibited very good catalytic activity (Scheme 1). Diverse aliphatic and benzylic alcohols were efficiently converted to imines, and a broad functional group tolerance was observed (Table 1). Moreover, mechanistic insight was also provided.

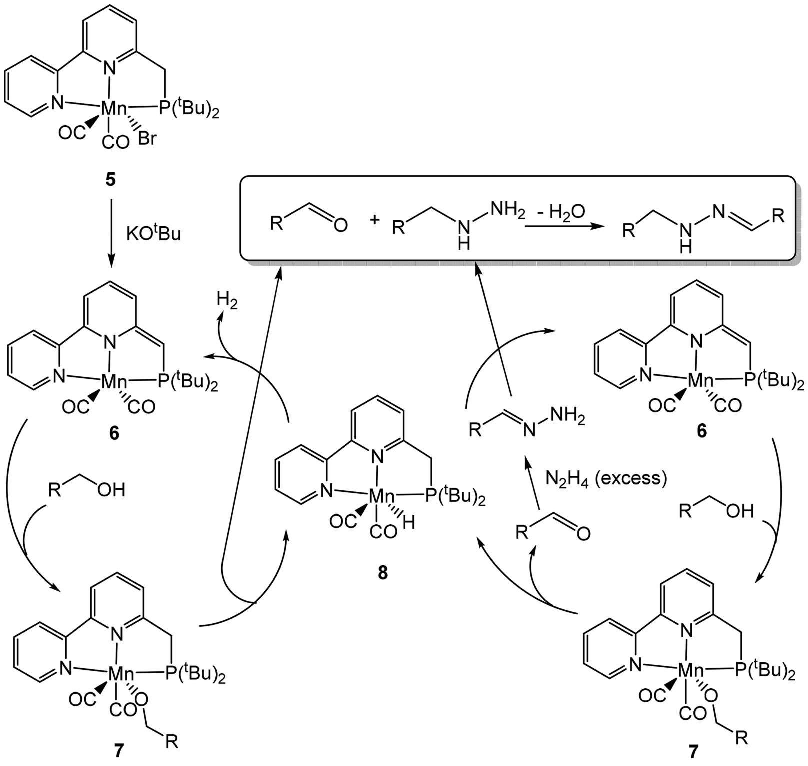
Table 1. Selected Examples of Dehydrogenative Coupling of Alcohols and Amines to Form Imines Catalyzed by 2 and the Imine Yields



Scheme 2. Deoxygenation of Primary Alcohols Using Mn Complex



Scheme 3. Proposed Reaction Mechanism for Hydrazone Synthesis Using Mn Complex 5

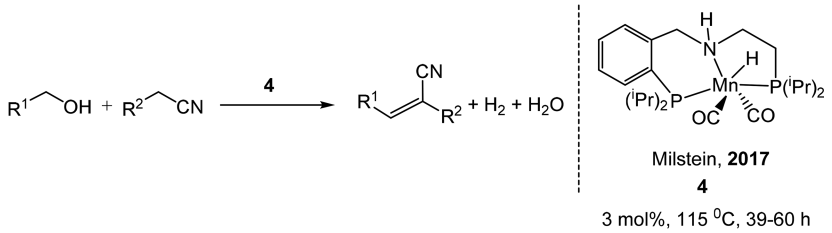


Soon after this report, the Kirchner group[18] showed that the related PNP manganese complex **3** is also useful as a catalyst for this reaction (Scheme 1).

2.2. Synthesis of Alkanes and Hydrazones. Milstein and co-workers[19,20] recently demonstrated that deoxygenation of primary alcohols and subsequent reaction with hydrazine lead to the formation of alkanes or N-substituted hydrazones, depending upon the manganese-based catalyst. When **4** was used as a precatalyst, the corresponding alkane was obtained as the main product (Scheme 2).[19] In the presence of **4**, the intermediate hydrazone undergoes a Wolff–Kishner reduction under the basic conditions to form the deoxygenated hydrocarbon. Interestingly, when complex **5** was employed in the catalytic reaction, hydrazones were formed in good yields.[20] Under the catalytic conditions, deprotonation of complex **5** by ^{t}BuOK yielded the active catalyst **6** bearing a diaromatized pincer ligand, which catalyzes alcohol dehydrogenation via metal–ligand cooperation (Scheme 3, left cycle). The aldehyde thus formed reacts with excess hydrazine to produce hydrazone, which undergoes hydrogenation of the C=N bond to form the N-substituted hydrazine through a borrowing hydrogen process (Scheme 3, right cycle). The latter reacts with an additional aldehyde molecule to form the N-substituted hydrazine. Under the catalytic conditions, both benzylic and aliphatic alcohols reacted smoothly.

2.3. α-Olefination of Nitriles. In 2017, Milstein and co-workers[21] reported the α-olefination of nitriles by alcohols catalyzed by the manganese complex **4** (Scheme 4). This is an unprecedented reaction for any metal complex, including noble metals. The reaction proceeds without any additives, such as bases, or hydrogen acceptor. A wide range of olefinic nitriles were obtained under the optimized reaction conditions with very good yields (up to 91%). In this reaction complex **4** liberates H$_2$ to form the corresponding amido complex, which

Scheme 4. *α*-Olefination of Nitriles with Alcohols Catalyzed by Mn Complex 4

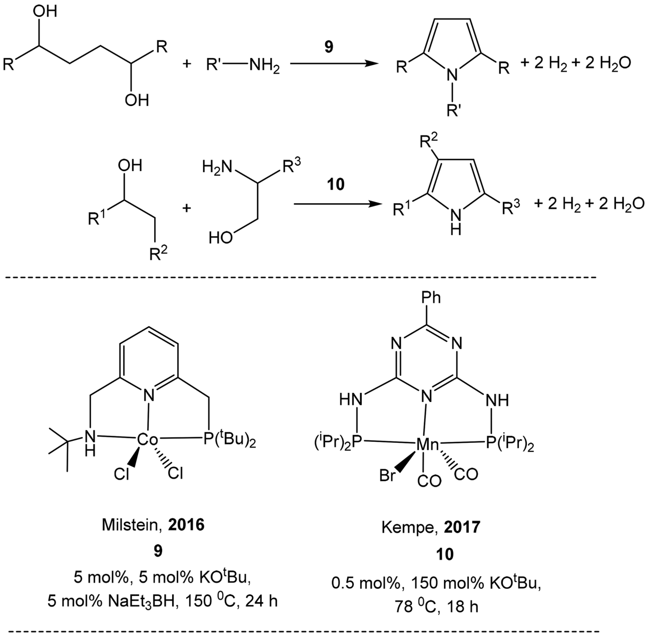


plays a dual role, as both a dehydrogenation catalyst and a base.

2.4. Synthesis of N-heterocycles. Aromatic N-heterocyclic compounds such as pyrroles, pyrimidines, pyridines, and quinolines are important classes of compounds, as they can be found in the building blocks of many natural products and pharmaceuticals. Over the past few decades, several new synthetic routes have been adopted for their synthesis. In particular, the acceptorless dehydrogenation of the alcohols followed by coupling with an amine derivative and subsequent dehydrogenation represents a sustainable synthesis of such families of heteroaromatics. A variety of noble-metal (mainly ruthenium and iridium)[22] catalysts have been developed for the synthesis of N-heterocycles using this strategy.

In 2016, Milstein and co-workers[23] reported the catalytic synthesis of substituted pyrroles starting from diols and amines using the cobalt pincer complex **9** (Scheme 5). The PNN(H)-Co complex **9** used in this study exhibited very good catalytic activity, and yields up to 93% of the substituted pyrroles were obtained. The reaction requires a base and hydride source in catalytic amounts, and it likely proceeds via a Co^I−H complex formed in situ. The reaction is applicable to a wide range of primary alkyl amines, benzylic amines, and aromatic amines and to primary and secondary diols. The same group also reported[24] the direct synthesis of benzimidazoles by dehydrogenative coupling of aromatic diamines and alcohols catalyzed by a cobalt pincer system. Very recently, Balaraman and co-workers[25] reported the SNS-cobalt pincer catalyzed acceptorless dehydrogenative coupling of unprotected amino alcohols with secondary alcohols, leading to the formation of pyrrole and pyridine derivatives.

Scheme 5. Synthesis of Pyrroles Catalyzed by Complexes 9 and 10



Milstein, 2016, **9**: 5 mol%, 5 mol% KO^tBu, 5 mol% $NaEt_3BH$, 150 °C, 24 h

Kempe, 2017, **10**: 0.5 mol%, 150 mol% KO^tBu, 78 °C, 18 h

Moreover, Kempe and co-workers[26] reported the efficient synthesis of pyrroles by dehydrogenative coupling of secondary alcohols with amino alcohols using precatalyst **10** (Scheme 5). Under the catalytic conditions, a variety of functional groups were tolerated and low catalyst loadings were used (0.5 mol %).

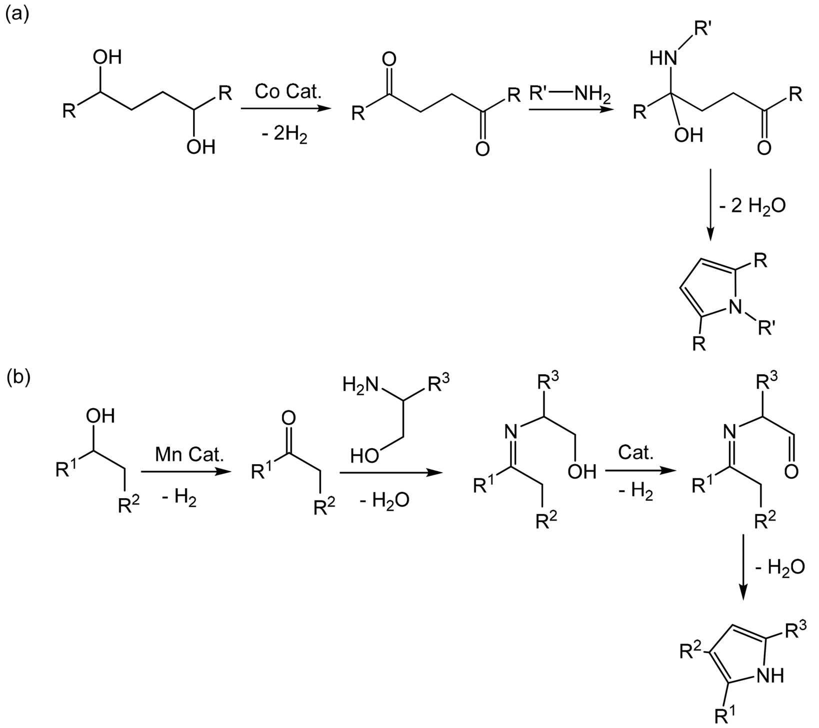
Mechanistically, formation of pyrrole catalyzed by cobalt and manganese complexes begins with dehydrogenation of the secondary alcohols to form ketones, which undergo coupling with amines or amino alcohols to provide hemiaminals or imines, respectively. Further dehydration yields pyrroles (Scheme 6a). On the other hand, the imine-alcohol intermediates initially undergo dehydrogenation to provide imino aldehyde intermediates (Scheme 6b), which upon base-catalyzed intramolecular condensation and aromatization provides the pyrroles as described in Scheme 6b.

Zhang and co-workers[27] reported the synthesis of quinoline derivatives by dehydrogenative coupling of 2-aminobenzyl alcohols with ketones using the cobalt complex **1** (Scheme 7). Furthermore, Kirchner[28] as well as Kempe[29] independently reported in 2016 the manganese-catalyzed syntheses of aromatic N-heterocycles (Scheme 7). Kirchner and co-workers showed that substituted quinolines can be synthesized through dehydrogenative coupling of 2-aminobenzyl alcohols and various secondary alcohols. As a catalyst they tested **11**, as well as similar complexes with a triazine backbone reported by Kempe. Interestingly, the N-methylated complex did not show any activity, which demonstrates the importance of the N−H group during the catalytic cycle. Under basic conditions, it is expected that the N−H proton undergoes deprotonation and the resulting amido complex activates the alcohol via metal−ligand cooperation.[18]

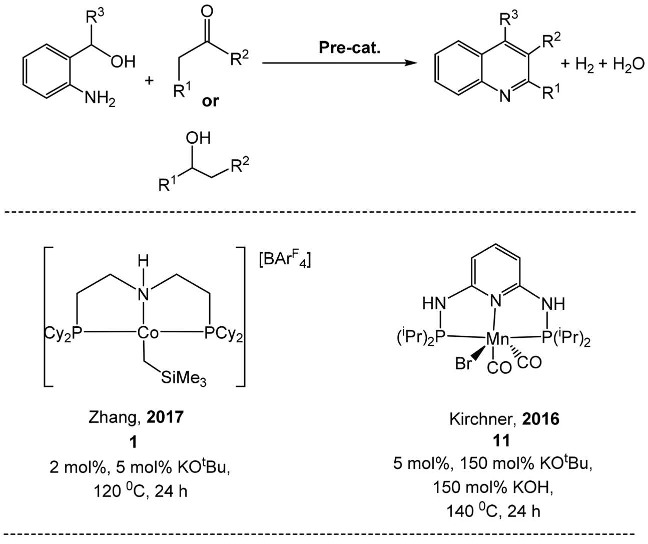
Furthermore, Kirchner[28] and Kempe[29] developed a three-component process for the production of substituted pyrimidines using benzamidine in the presence of a primary and a secondary alcohol (Scheme 8). Moreover, Kempe reported a consecutive four-component reaction for the synthesis of tetrasubstituted pyrimidines using a similar protocol (Scheme 8). Several manganese catalysts having a triazine pincer ligand were additionally tested by Kempe and co-workers for the synthesis of pyrimidines, the manganese complex **10** being the most efficient. Similarly, Kirchner and co-workers found that **11** is an efficient catalyst for the same transformation. Both groups showed wide applicability of their manganese catalysts and demonstrated the synthesis of several substituted pyrimidines with good isolated yields. While the Kirchner group concentrated on aromatic alcohols, the Kempe group used several aliphatic primary as well as secondary alcohols.

2.5. Borrowing Hydrogen Reactions. Borrowing hydrogen, also known as hydrogen autotransfer, is a process in

Scheme 6. Proposed Mechanism for the Formation of Pyrroles: (a) Dehydrogenation of Diol Followed by Coupling with Amine Catalyzed by Complex 9 and (b) Dehydrogenation Alcohol Followed by Coupling with Amino Alcohol Catalyzed by Complex 10



Scheme 7. Synthesis of Quinolines Catalyzed by Complexes 1 and 11



which hydrogen or metal hydrides formed during an initial dehydrogenation step are involved in a consecutive hydrogenation of an unsaturated intermediate formed via a condensation step. Interestingly, the dehydrogenation and the borrowing hydrogen processes can be efficiently mediated by the same catalyst.[5c,11b] The limited reactivity of alcohols toward nucleophiles can be readily overcome using this synthetic route. Nitrogen-containing compounds, ranging from primary amines to heterocycles, were obtained using the metal-catalyzed, alcohol-borrowing hydrogen pathway.

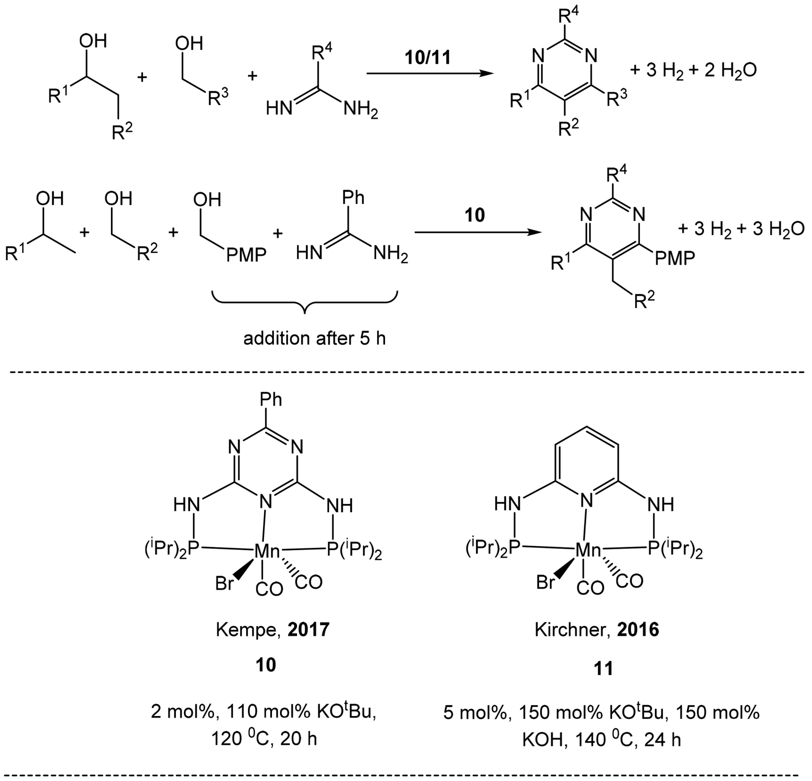
2.5.1. N-alkylation Reaction of Amines. Formation of C−N bonds is a fundamentally important reaction for the synthesis of pharmaceuticals and fine chemicals. Over the past decades, several catalytic methods have been employed for the construction of C−N bonds, such as classic nucleophilic substitutions,[30] Buchwald−Hartwig coupling,[31] Ullmann reaction,[32] and hydroamination reactions.[33] Recently, significant progress has been made using various borrowing-hydrogen methodologies for the environmentally benign formation of C−N bonds using different metals.

In 2015, Kempe and co-workers[34] first reported the cobalt-catalyzed N-alkylation of aromatic amines with primary alcohols using the pincer complex **12** (Scheme 9). Various functional groups are tolerated under relatively mild conditions (80 °C) using 2 mol % low precatalyst loading. Both aliphatic and aromatic alcohols exhibited very good catalytic activity with the aromatic amines (Table 2). The reaction works well with unsymmetrically substituted diamines as well (up to 91%).

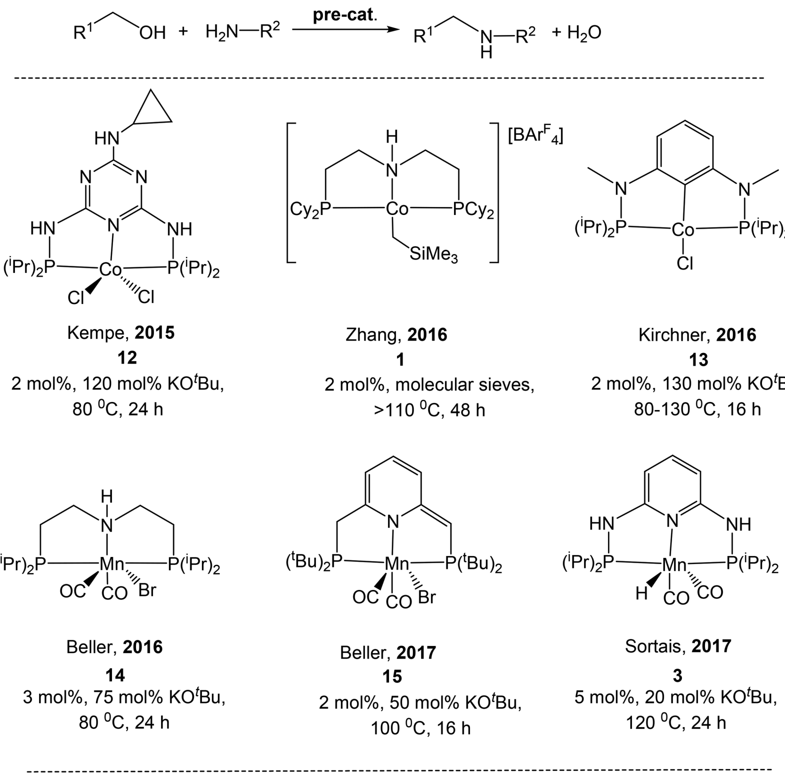
Soon after this report Zhang and co-workers[35] as well as Kirchner and co-workers[36] showed that the PNP- and PCP-type pincer cobalt complexes **1** and **13**, respectively, can be used for the N-alkylation reaction with primary alcohols (Scheme 9). Interestingly, the cobalt complex **1** was catalytically active with both aliphatic and aromatic amines, but **13** was active only in the case of aromatic amines.

Moreover, Zhang and co-workers[37] also reported the N-alkylation of amines with other amines (rather than alcohols) through the hydrogen-borrowing strategy. The PNP-Co(II) complex **1** exhibited very good catalytic activity, and a range of amine substrates were converted to the corresponding products through hetero- or homocoupling between amines with the expulsion of NH_3. Furthermore, cyclic *sec*-amines can be easily obtained starting from diamine precursors, making it a convenient synthetic route. In this regard, Balaraman and co-workers[38] recently reported a phosphine-free NNN cobalt pincer complex for the alkylation of anilines.

Scheme 8. Synthesis of Pyrimidines Catalyzed by Complexes 10 and 11



Scheme 9. N-alkylation of Amines Using Co and Mn Catalysts by Borrowing Hydrogen Method



Beller and co-workers[39] reported the first manganese-catalyzed alkylation of amines with alcohols using **14** as the precatalyst (Scheme 9). The reaction was carried out under mild conditions with a diverse range of products, including heteroarenes, olefins, halides, and thioethers (Table 3). Unsaturated primary amines were chemoselectively converted into the corresponding secondary amines. Primary alcohols utilized include not only (hetero)aromatic alcohols but also aliphatic alcohols with varying chain lengths, and the reaction tolerates diverse functional groups. Interestingly, methanol also

Table 2. Selected Examples of N-alkylation of Amines Catalyzed by 12

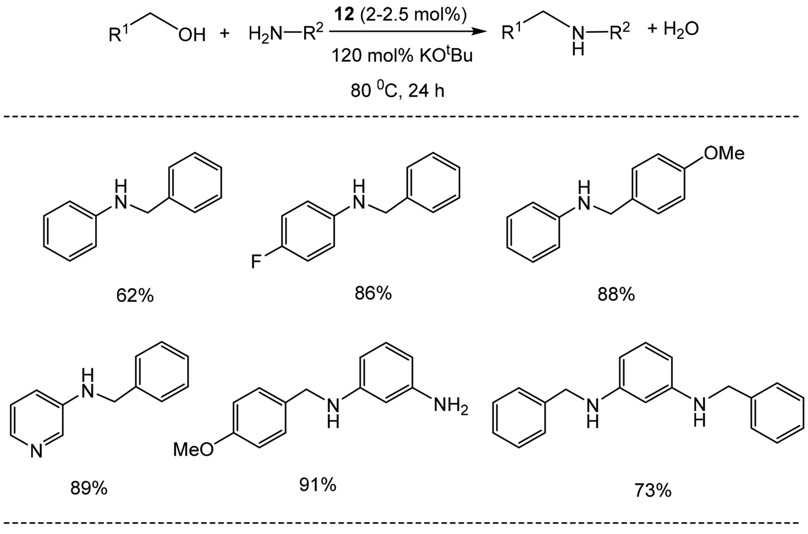
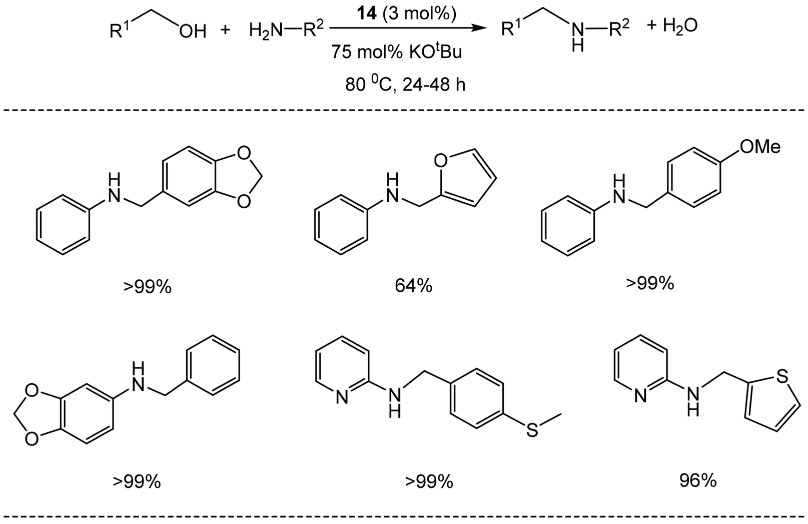
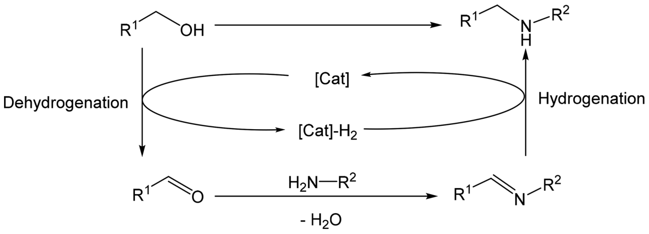


Table 3. Selected Examples of N-Alkylation of Amines Catalyzed by 14



Scheme 10. General Scheme for the N-alkylations of Amines by Borrowing Hydrogen Methodology



reacts, producing *N*-methylamines, although higher temperatures (100 °C) and 1 equiv of base were required in comparison to the previous reaction. In followup work, the same group further optimized the synthesis by using the manganese complex **15**, bearing a dearomatized ligand, which permitted milder conditions.[40] Similarly, Sortais and co-workers[41] showed that the related manganese complex **3** can efficiently catalyze the reaction as well.

In these reactions, the catalyst first dehydrogenates the alcohol and the resulting aldehyde undergoes condensation with the amine to form an imine. The catalyst then hydrogenates the imine using the borrowed hydrogen to produce the amine (Scheme 10).

Recently, Kirchner and co-workers[42] reported the manganese-catalyzed three-component aminomethylation of activated aromatic compounds including naphthols, phenols, pyridines, indoles, carbazoles, and thiophenes in combination with amines and MeOH (Scheme 11). These reactions proceed with high atom efficiency via a sequence of dehydrogenation and condensation steps which give rise to selective C−C and C−N bond formations, liberating hydrogen and water. Diverse functional groups are tolerated under the catalytic conditions, and a total of 28 different aminomethylated products were synthesized with isolated yields of up to 91% using precatalyst **3**.

2.5.2. C-alkylation Reaction. Apart from the N-alkylation of amines by alcohols/amines to form the C−N bonds, construction of C−C bonds through C-alkylation is important for the sustainable synthesis of various important compounds. Upon alcohol dehydrogenation, the generated carbonyl compounds can act as electrophiles and undergo coupling reactions with nucleophiles to generate unsaturated intermediates; further

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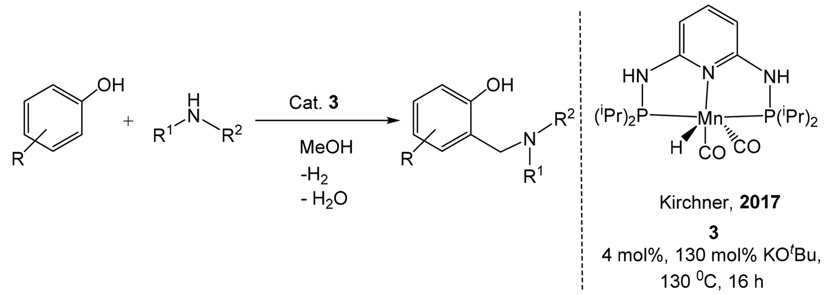
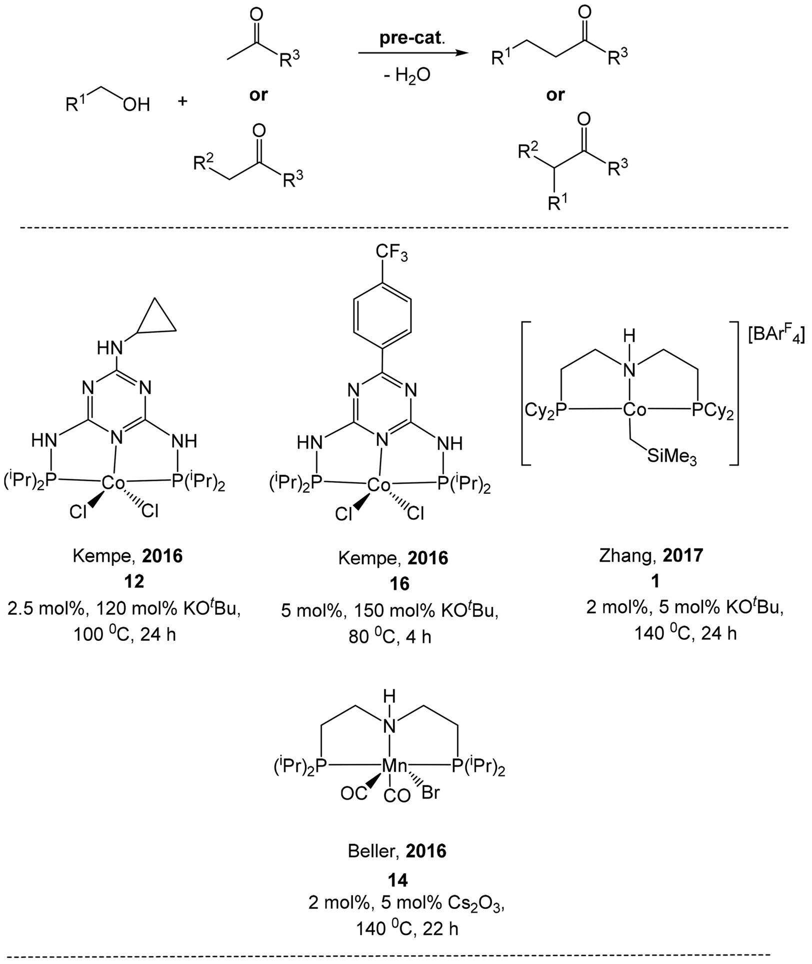
Scheme 11. Aminomethylation of Arenes Using Methanol and Amines with Mn Catalyst



Scheme 12. C-alkylation of Amides, Esters, and Ketones with Primary Alcohols Using Co and Mn Catalysts



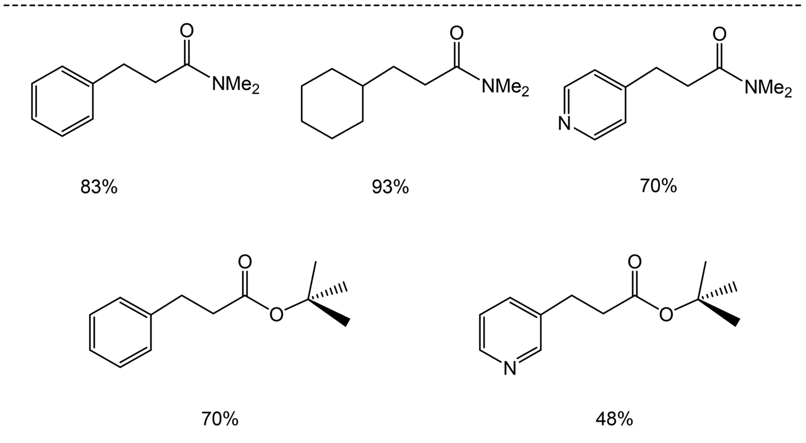
hydrogenation by using hydrogen, borrowed from the alcohols in the first step, provides the product.

In 2016, Kempe reported[43] the first cobalt-catalyzed C-alkylation of unactivated amides and esters with alcohols (Scheme 12). Amide alkylation products were obtained in up to 93% isolated yields using **12** as precatalyst (2.5 mol %), nearly the same as reported for an Ir catalyst,[44] but under milder reaction conditions and with application of less base (100 °C and 1.2 equiv of KO^tBu). Moreover, the demanding ester alkylation reaction produced the corresponding products in moderate to good yields (up to 82%) using precatalyst **16** (Table 4). Furthermore, the amide alkylation products were subsequently converted into compounds with other functional groups (ketone, aldehyde), demonstrating the value of the alkylated products obtained by this synthetic route.

Zhang and co-workers[27] reported the cobalt-catalyzed α-alkylation of ketones with primary alcohols using **1** as a catalyst (Scheme 12). A broad range of ketone and alcohol substrates was employed, leading to the isolation of alkylated ketones with yields up to 98%. Subsequently, Kempe and co-workers[45] reported the cobalt-catalyzed alkylation of secondary alcohols with primary alcohols. The catalysis proceeds under relatively mild conditions with a broad substrate scope. Interestingly, aliphatic alcohols also undergo the coupling reaction under basic reaction conditions.

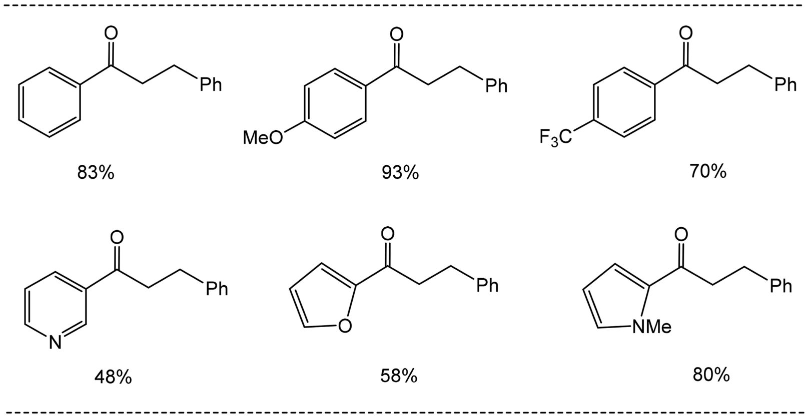
Beller and co-workers[46] reported the catalytic α-alkylation of ketones with primary alcohols using the manganese complex **14** with catalytic amounts of base (Scheme 12). Diverse functional groups were tolerated, including substituted aryl, heterocyclic, and aliphatic ketones, albeit in lower yield (Table 5).

Table 4. Selected Examples of C-alkylation of Alcohols and Esters Catalyzed by 12[a] and 16[b]



[a]Reaction conditions: alcohol (1 mmol), amide (2 mmol), *t*-BuOK (1.2 mmol), **12** (0.025 mmol), THF (4 mL), 100 °C, 24 h. [b]Reaction conditions: alcohol (1 mmol), *tert*-butyl acetate (4 mmol), *t*-BuOK (1.5 mmol), toluene (1 mL), **16** (5 mol %), 80 °C, 4 h.

Table 5. Selected Examples of C-alkylation of Ketones Catalyzed by 14[a]



[a]Reaction conditions: **14** (2 mol %),Cs_2CO_3 (5 mol %), tert-amyl alcohol, 140 °C, 22 h.

Additionally, the reaction of different aromatic and aliphatic alcohols with acetophenone or 2-oxindole resulted in very high selectivity with good to very good yields even in the presence of secondary amines. Furthermore, functionalization of the hormones estrone 3-methyl ether and testosterone was achieved with different alcohols. Participation of an intramolecular amidate-assisted alcohol-dehydrogenation process was proposed.

Similarly, Kempe reported[26] the manganese- catalyzed four-component synthesis of pyrimidines using **10** as a precatalyst. The initial step in this synthesis involves α-alkylation of a secondary alcohol with a primary alcohol (Scheme 12).

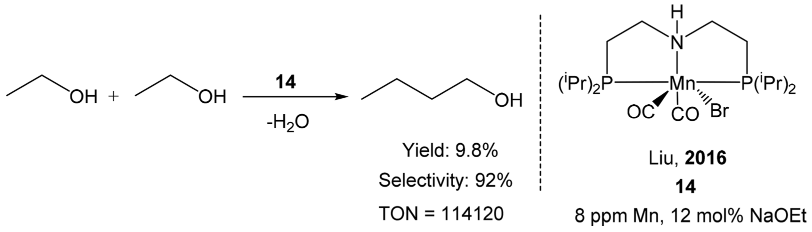
2.5.3. Synthesis of Biofuel. The quest for alternative energy sources has gained significant attention in recent years due to energy security and environmental protection issues.[47] Biofuels produced from renewable biomass are recognized as sustainable alternatives to gasoline and cause low environmental damage. Biofuels offer much promise in these frontiers and are being explored as alternatives for the diminishing fossil fuels. Currently, ethanol is being probed as a sustainable alternative fuel to conventional gasoline. However, butanol is more attractive than ethanol, as it has an energy density closer to that of gasoline (90%),[48] is noncorrosive to the engine parts, and is immiscible with water. Hence, upgrading ethanol into butanol is considered to be a promising strategy for the production of improved alcohol biofuel from renewable biomass.[49] In this regard, the Guerbet reaction can be utilized for the generation of longer-chain alcohols from ethanol. Several late-transition-metal catalysts have been developed over the past few years that have exhibited very high catalytic activity and turnover numbers (up to 18209) for this transformation reaction.[50]

Liu and co-workers[51] reported in 2017 the first homogeneous manganese-catalyzed conversion of ethanol to *n*-butanol using **14** as a precatalyst (Scheme 13). The activity of the manganese complex used in this study is comparable to that of noble-metal catalysts. The developed reaction represents a sustainable synthesis of 1-butanol with a very high turnover number of 114120 (at 11.2% conversion, 9.8% yield of butanol) and high turnover frequency (>3000 h^{-1}) at 160 °C. Soon after this report, the Jones group[52] showed that related PNP ligand stabilized manganese complexes can also be useful for this transformation reaction.

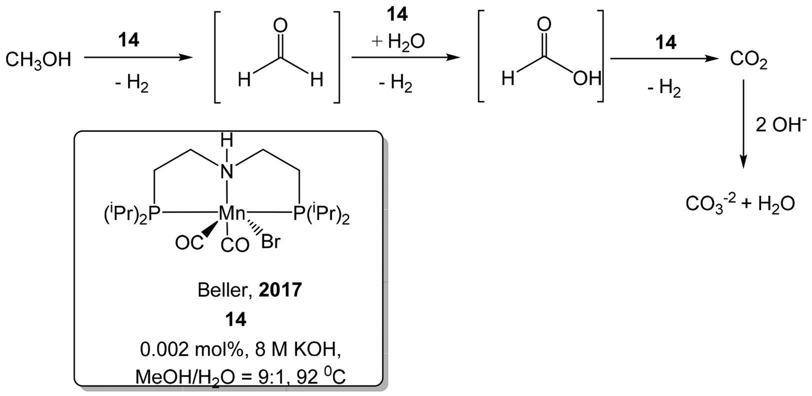
2.6. Dehydrogenation of Methanol.

Reforming of methanol by water to molecular hydrogen and carbon dioxide is an important transformation with respect to the implementation of hydrogen and methanol economies. Methanol is considered to be a promising hydrogen carrier since it contains high hydrogen capacity, and as a liquid under ambient conditions it significantly simplifies transportation and handling. Catalytic dehydrogenation of methanol is more challenging in comparison to that of the higher alcohols. While the

Scheme 13. Upgrade of Ethanol to 1-Butanol Using Mn Catalyst **14**



Scheme 14. Dehydrogenation of Methanol/Water Mixtures to H_2 and CO_2 or CO_3^{2-} Using Mn Catalyst **14**



heterogeneous catalysts used for the same transformation require harsh reaction conditions (high temperature or high pressure or both), relatively mild reaction conditions and low catalyst loading were required using homogeneous late-transition-metal complexes.[53] Apart from these precious-metal catalysts, a handful of iron complexes are also known.[54]

Recently, Beller and co-workers[55] reported the first manganese-catalyzed dehydrogenation of methanol/water mixtures using the pincer complex **14** as a precatalyst (Scheme 14). It was postulated that, in the presence of **14**, methanol initially undergoes dehydrogenation to give formaldehyde. Subsequently, addition of water to formaldehyde forms methanediol, which in turn undergoes dehydrogenation to formic acid. Formic acid undergoes dehydrogenation to CO_2 and H_2, as demonstrated by Tondreau and Boncella.[56] The manganese catalyst **14** demonstrated excellent long-term stability, and a turnover number of more than 20000 was obtained under relatively mild conditions. Furthermore, hydrogen carriers, such as ethanol, paraformaldehyde, and formic acid, were also successfully dehydrogenated under the catalytic conditions.

In this regard, Yang and co-workers[57] provided a detailed computational understanding of the cobalt catalyzed dehydrogenation of ethanol to acetaldehyde and hydrogen.

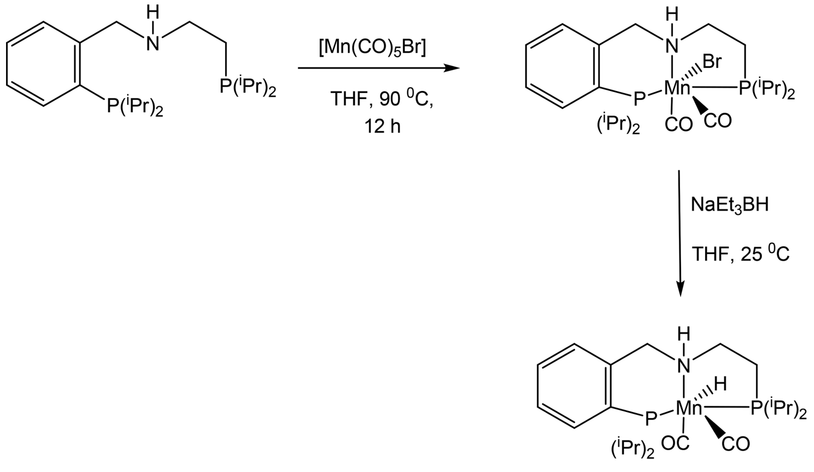
2.7. Dehydrogenative N-formylation of Amines by Methanol. Formamides serve as valuable intermediates in the synthesis of pharmaceuticals, agrochemicals, dyes, and fragrances.[58] Moreover, they are also used as industrial solvents and are useful reagents for the Vilsmeier−Haack reaction. Among the several methods available for their synthesis,[59] the acceptorless dehydrogenative coupling of methanol with a suitable amine precursor is considered to be an attractive route to convert primary and secondary amines into the corresponding formamides.

Recently, Milstein and co-workers[60] described the first manganese-catalyzed acceptorless dehydrogenative coupling of methanol and amines to form formamides. The manganese complex **17** was synthesized in a simple two-step process starting from the PNP pincer ligand and $[Mn(CO)_5Br]$ (Scheme 15). The catalytic reaction tolerates diverse functional groups, and aliphatic as well as benzylic amines were formylated in good yields (Table 6). The reaction proceeds without any additives using the manganese pincer catalyst under homogeneous conditions (Scheme 16). A plausible mechanism was provided on the basis of the rare direct observation of an intermediate that was formed by O−H bond activation of methanol by metal−ligand cooperation.

2.8. Synthesis of Cyclic Imides by Dehydrogenative Coupling of Diols and Amines. Milstein and co-workers[61] reported the first example of base-metal-catalyzed dehydrogenative coupling of diols and amines to form cyclic imides (Scheme 17). The reaction is catalyzed by the manganese pincer complex **18** and forms hydrogen gas as the sole byproduct, making the overall process atom-economical and sustainable. Diverse N-substituted cyclic imides can be obtained efficiently using this synthetic route. A detailed mechanistic investigation suggests the formation of a hemiaminal intermediate, which upon dehydrogenation is converted to the cyclic imide.

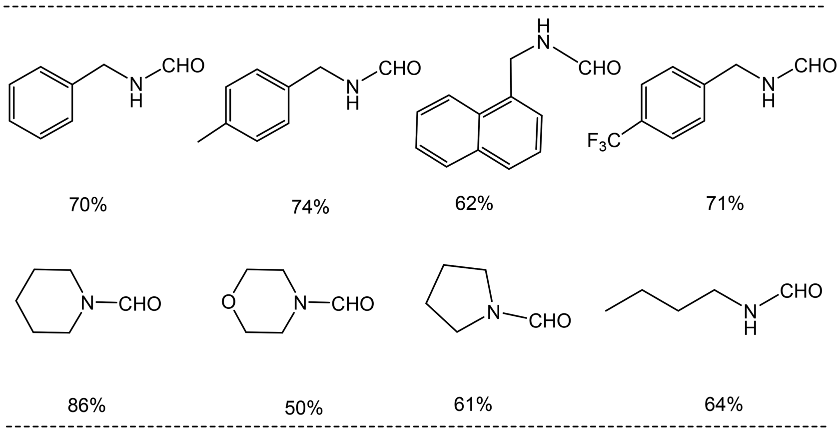
2.9. Synthesis of Amides by Dehydrogenative Coupling of Amines with either Alcohols or Esters. Formation of the amide bond is one of the most fundamental reactions with respect to chemistry and biology.[62] Compounds containing amide groups are prevalent in both synthetic and natural products and are very important in the chemical and pharmaceutical industries. Conventional methods for the synthesis of amides involve the reaction of either carboxylic acids or their activated derivatives with amines in the presence of promoters, thus generating stoichiometric amounts of waste.[63] In 2007, Milstein and co-workers[64] reported the fundamentally new synthesis of amides by dehydrogenative coupling of alcohols and amines, catalyzed by 0.1 mol % of a dearomatized PNN ruthenium pincer complex under neutral conditions, hydrogen

Scheme 15. Synthesis of Mn(I) Complex 17



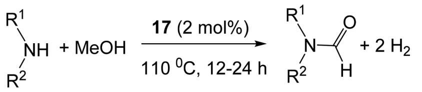
17

Table 6. Selected Examples of N-formylation of Amines with Methanol Catalyzed by 17[a]



[a]Reaction conditions: amine (0.5 mmol), MeOH (1 mL), **17** (0.01 mmol), 110 °C, 12−24 h.

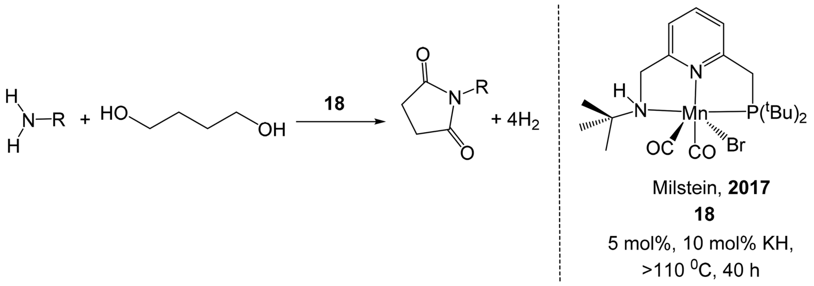
Scheme 16. Dehydrogenative Formylation of Amines Using Methanol with Mn Catalyst 17



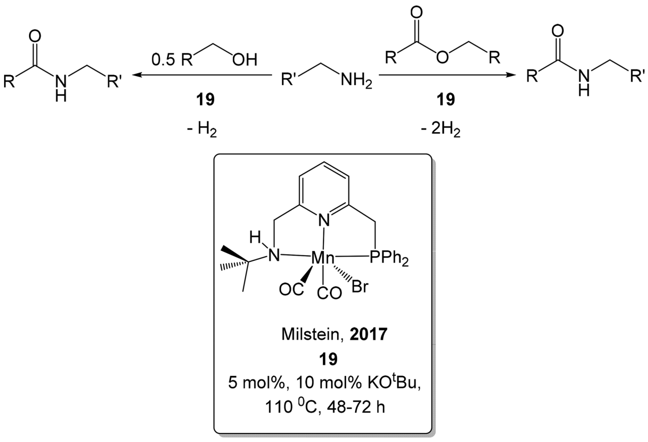
gas being generated as the sole byproduct. This reaction opened up a new area for the atom-economical and environmentally benign synthesis of amides, and several precious-metal-based catalysts were subsequently reported.[65]

In 2017, Milstein and co-workers[66] demonstrated the first base-metal-catalyzed synthesis of amides by the coupling of primary amines with either alcohols or esters (Scheme 18). The reaction is environmentally benign and proceeds cleanly with liberation of H_2. Using precatalyst **19**, a wide variety of either linear or branched aliphatic alcohols undergo the amidation reaction efficiently with benzylamines bearing various substituents (Table 7). Notably, poor reactivity was observed when benzyl alcohols were employed (as an alcohol part) due to the formation of imines as side products from the condensation of alcohols and amines. Initially, dehydrogenation of the primary alcohol leads to the formation of the carbonyl compound, which undergoes reaction with the amine to produce the corresponding hemiaminal intermediate, followed by dehydrogenation to form the amide (Scheme 19).

Scheme 17. Synthesis of Cyclic Imides Catalyzed by Mn Catalyst 18



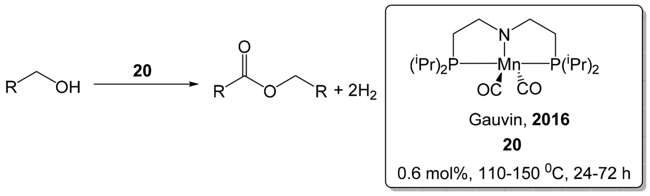
Scheme 18. Synthesis of Amides by Dehydrogenative Coupling of Amines with Either Alcohols or Esters Catalyzed by Mn Catalyst 19



Furthermore, treatment of symmetrical esters with 2 equiv of amines also results in the formation of amides with the elimination of hydrogen (Scheme 19). Both aliphatic and aromatic esters undergo this reaction in good to excellent yields (50−95%). The ester amidation reaction was suggested to proceed via initial coupling of the ester and amine to form amide and alcohol, followed by reaction of the generated alcohol with the remaining amine to produce the amide, as suggested previously.

2.10. Ester Synthesis by Dehydrogenative Coupling of Alcohols. Gauvin and co-workers[67] recently showed that the manganese complex **20** catalyzes the dehydrogenative coupling of alcohols to form the corresponding esters with H_2 evolution (Scheme 20). Various aliphatic and aromatic alcohols undergo this reaction under relatively low catalyst loading. A detailed mechanistic pathway of this reaction was proposed.

Scheme 20. Synthesis of Esters via Dehydrogenative Coupling of Alcohols Catalyzed by 20

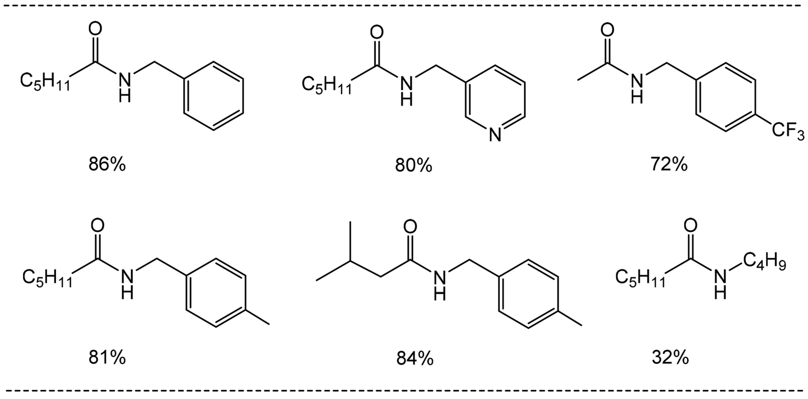


2.11. Synthesis of N-heteroaromatics by Dehydrogenation of Amines. Jones and co-workers reported[68] the PNP pincer cobalt catalyzed acceptorless dehydrogenation of the six-membered tetrahydroquinoline to the quinolone (Scheme 21). The reaction proceeds at relatively high temperature (150 °C) with 10 mol % catalyst (**1**) loading. Interestingly, hydrogen was produced as the sole byproduct and good to excellent yields of the corresponding aromatic products (up to 98%) were obtained. Additionally, five-membered 2-methylindoline, 2,6-dimethylpiperidine, and 1,2,3,4-tetrahydroquinoxaline were also dehydrogenated to the corresponding aromatic products using **1** as catalyst.

3. HYDROGENATION REACTIONS

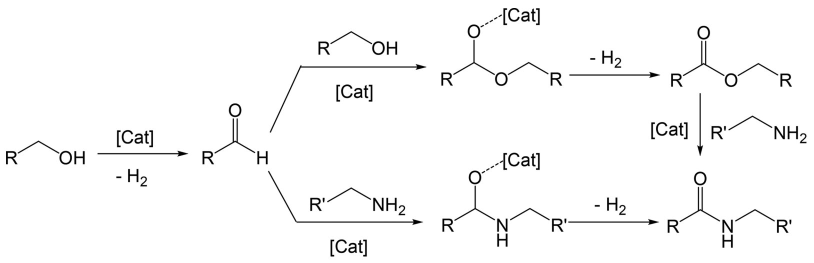
Catalytic hydrogenation using molecular hydrogen is one of the most important methodologies in the field of homogeneous catalysis. It allows atom-efficient and clean functional group transformations, enabling isolation of intermediates for the pharmaceutical and chemical industries. Since the pioneering work of Noyori[69] on the catalytic hydrogenation of carbonyl compounds, much progress in catalytic hydrogenations has been made, mostly using homogeneous noble-metal complexes.[5c,d]

Table 7. Selected Examples of Amidation by Dehydrogenative Coupling of Alcohols and Amines Catalyzed by 19[a]

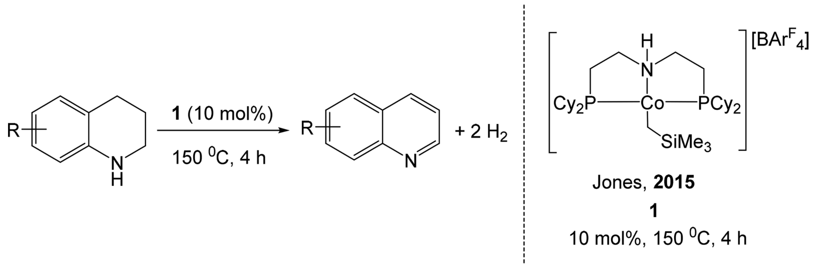


[a]Reaction conditions: alcohol (0.5 mmol), amine (0.5 mmol), **19** (5 mol %), KOtBu (10 mol %), 110 °C, 48 h.

Scheme 19. General Pathway for the Dehydrogenative Amidation Reaction Catalyzed by Metal Complexes



Scheme 21. Acceptorless Dehydrogenation of N-heterocycles Catalyzed by 1

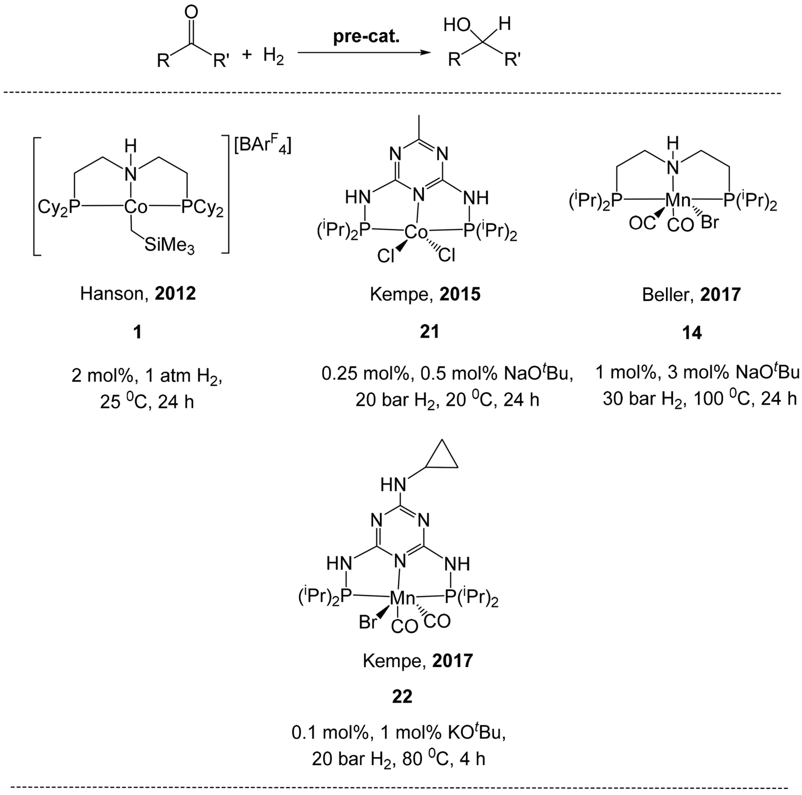


Jones, **2015**

1

10 mol%, 150 ⁰C, 4 h

Scheme 22. Hydrogenation of Ketones Catalyzed by Co and Mn Complexes



Hanson, **2012**

1

2 mol%, 1 atm H_2, 25 ⁰C, 24 h

Kempe, **2015**

21

0.25 mol%, 0.5 mol% NaO^{t}Bu, 20 bar H_2, 20 ⁰C, 24 h

Beller, **2017**

14

1 mol%, 3 mol% NaO^{t}Bu, 30 bar H_2, 100 ⁰C, 24 h

Kempe, **2017**

22

0.1 mol%, 1 mol% KO^{t}Bu, 20 bar H_2, 80 ⁰C, 4 h

Significant progress in the hydrogenation of a variety of classes of unsaturated compounds catalyzed by complexes of earth-abundant metals has been made in recent years, including seminal reports on iron-based hydrogenation catalysts for various types of multiple bonds (C−heteroatom).[6] In this review, the recent developments in hydrogenation chemistry using cobalt and manganese pincer complexes are discussed.

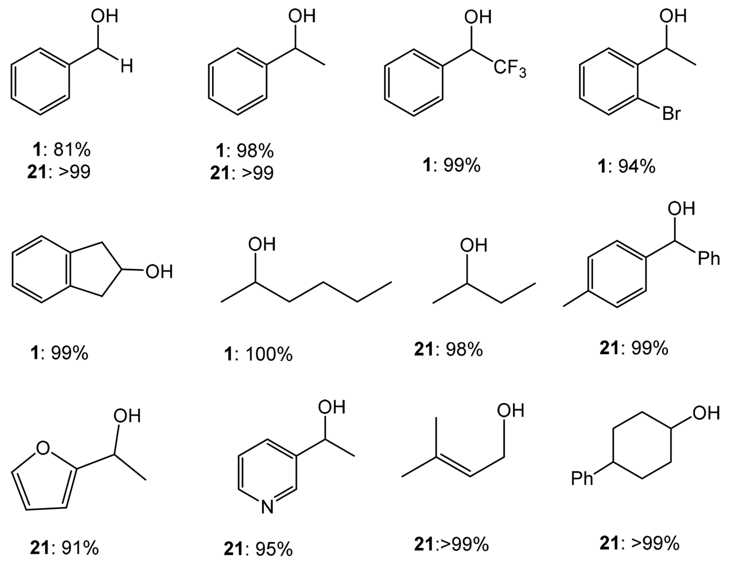
3.1. Hydrogenation of Aldehydes and Ketones. The homogeneously catalyzed hydrogenation of carbonyl compounds using dihydrogen, accomplished predominantly by complexes of noble metals, such as ruthenium, rhodium, and iridium, constitutes an important transformation in industrial organic processes.[70] In contrast, homogeneous hydrogenation catalysis by earth-abundant-metal complexes is much less developed. In the past few years, a number of iron complexes were developed for the catalytic hydrogenation of carbonyl compounds to the corresponding alcohols,[9a] while reports of homogeneous hydrogenation catalysts based on cobalt and manganese are still limited.

In 2012, Hanson and co-workers[71] reported the first cobalt pincer catalyzed hydrogenation of carbonyl compounds (Scheme 22). Catalyst **1** functions under mild conditions (25−60 °C) under 1 atm of H_2. Both aliphatic and aromatic carbonyl compounds were hydrogenated with low precatalyst loading (2 mol %) (Table 8). Later, Wolf, von Wangelin, and co-workers[72] reported the hydrogenation of carbonyl compounds catalyzed by arene cobalt complexes.

Furthermore, in 2015 Kempe and co-workers[73] reported the triazine ligand based Co(II) precatalyst **21** for the hydrogenation of carbonyl compounds (Scheme 22). The reaction took place using low loading (0.25 mol %) of the cobalt dichlorido precatalysts in addition to a catalytic amount of base (0.5 mol %). Both aldehydes and ketones of different kinds (dialkyl, aryl alkyl, diaryl) were hydrogenated quantitatively under mild conditions (Table 8). Interestingly, the catalyst demonstrated high chemoselectivity and preferentially catalyzed the hydrogenation of C═O bonds in the presence of C═C bonds. This selectivity is inverse to that of existing cobalt catalysts and surprising because of the potential directing influence of a hydroxyl group in C═C bond hydrogenation.

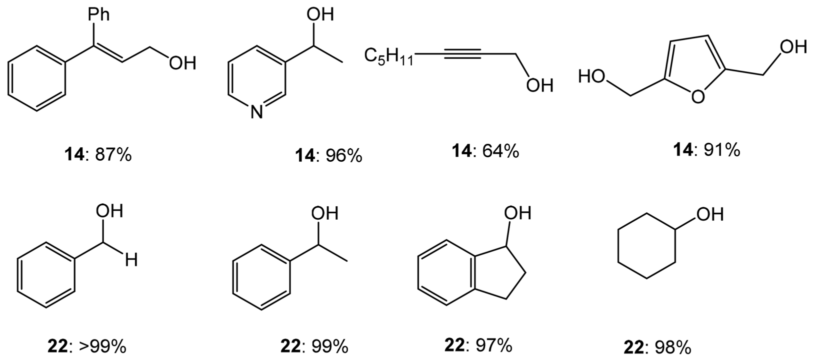
In addition to this, recently Beller and co-workers as well as Kempe and co-workers independently reported the manganese pincer catalyzed hydrogenation of carbonyl compounds (Scheme 22). Beller[74] showed that the manganese complex **14**

Table 8. Selected Examples of Hydrogenation Products of Aldehydes and Ketones Catalyzed by **1**[a] and **21**[b]



[a] Reaction conditions: carbonyl compound (0.5 mmol), **1** (2 mol %), H_2 (1 atm), 25 °C, 24 h. [b] Reaction conditions: carbonyl compound (3 mmol), **21** (0.25 mol %), NaOtBu (0.5 mol %), H_2 (20 bar), 20 °C, 24 h.

Table 9. Selected Examples of Hydrogenation Products of Aldehydes and Ketones Catalyzed by **14**[a] and **22**[b]



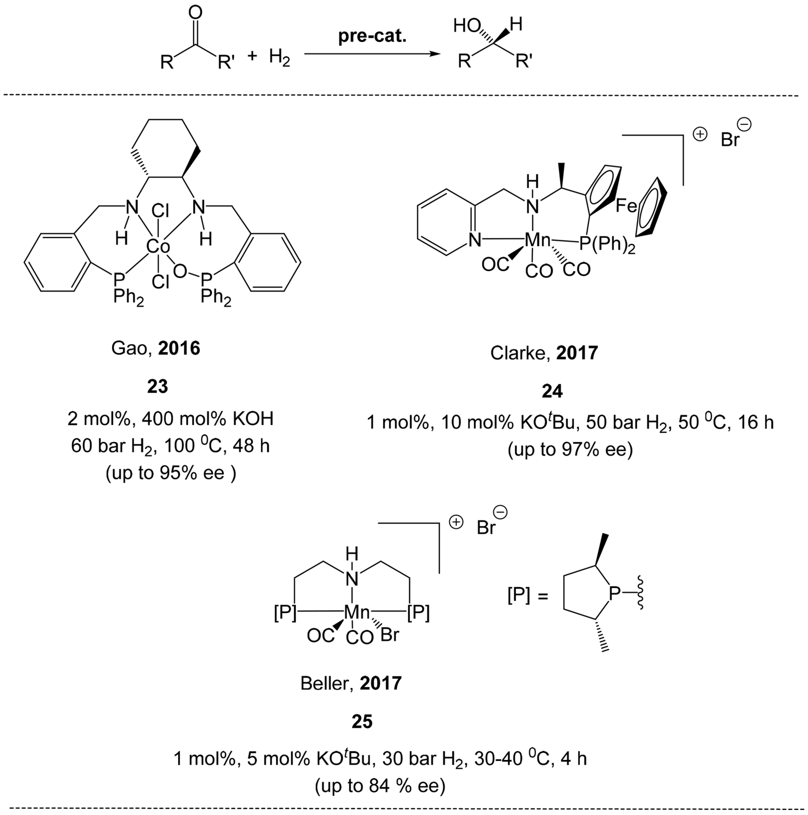
[a] Reaction conditions: carbonyl compound (1 mmol), **14** (1 mol %), NaOtBu (3 mol %)H_2 (10−30 bar), 60−100 °C, 24 h. [b] Reaction conditions: carbonyl compound (3 mmol), **22** (0.1−1 mol %), NaOtBu (1 mol %), H_2 (20 bar), 80 °C, 4 h.

in conjunction with NaO^{t}Bu catalyzes the hydrogenation of a number of aldehydes and ketones to the corresponding primary and secondary alcohols (Table 9). The reaction resulted in good to excellent yields of the alcohols under relatively mild conditions. A variety of reducible functional groups, such as ester groups, C═C double bonds, and lactams, were tolerated under the catalytic conditions. Apart from aromatic and aliphatic aldehydes, *α*,*β*-unsaturated substrates including some natural products such as citronellal and 5-(hydroxymethyl)-furfural were also successfully reduced under the catalytic conditions.

Furthermore, Kempe[75] developed the triazine-based manganese complex **22**, which was used as a precatalyst for the reduction of aldehydes and ketones (Scheme 22). The activity of complex **22** was found to be superior to that reported by Beller using complex **14**. The manganese complex **22** catalyzes the hydrogenation of acetophenone under relatively mild conditions (80 °C, 20 bar of H_2, 4 h) using low catalyst loading (0.1 mol %). Moreover, a broad substrate scope was observed, including differently substituted aromatic ketones and aldehydes, using catalyst loadings up to 1 mol % (Table 9). Linear as well as cyclic aliphatic ketones were hydrogenated under the optimized conditions. As a consequence of the milder conditions, improved reactivity and selectivity using unsaturated ketones were achieved, where terminal as well as internal alkenes remained intact. Recently, Kirchner and co-workers[76] reported the manganese-catalyzed hydrogenation of aldehydes at room temperature under base-free conditions using low catalyst loadings (0.1 to 0.05 mol %) under 50 bar of hydrogen pressure (TONs of up to 2000).

In 2016, Gao and co-workers[77] showed that cobalt complexes based on a tetradentate PNNP ligand can be used for the asymmetric hydrogenation of ketones (Scheme 23). The hydrogenation reaction required 60 bar of H_2 pressure, and the corresponding chiral alcohols were obtained with up to 99% yield and 95% ee using complex **23**. Furthermore, Clarke and co-workers[78] demonstrated the first asymmetric hydrogenations of ketones catalyzed by chiral, ferrocene- substituted

Scheme 23. Asymmetric Hydrogenation of Ketones Catalyzed by Chiral Co and Mn Complexes



Gao, **2016**

23

2 mol%, 400 mol% KOH
60 bar H_2, 100 °C, 48 h
(up to 95% ee)

Clarke, **2017**

24

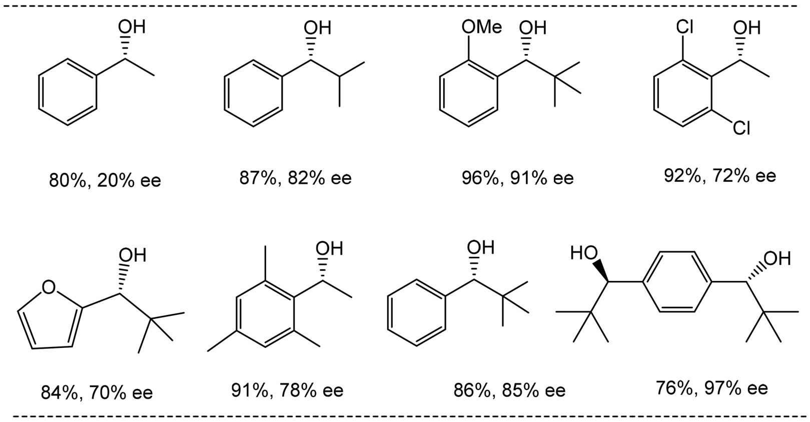
1 mol%, 10 mol% KO^{t}Bu, 50 bar H_2, 50 °C, 16 h
(up to 97% ee)

Beller, **2017**

25

1 mol%, 5 mol% KO^{t}Bu, 30 bar H_2, 30-40 °C, 4 h
(up to 84 % ee)

Table 10. Selected Examples of Asymmetric Hydrogenation of Ketones Catalyzed by 24[a]



[a] Reaction conditions: **24** (1 mol %), KOtBu (10 mol %), H_2 (50 bar), 50 °C, 16 h.

PNN manganese complex **24**. Complex **24** exhibited high catalytic activity and enantioselectivity (up to 97%) for the hydrogenations of a large variety of ketones under 50 bar of H_2 pressure (Scheme 23). Both electron-donating and electron-withdrawing substituents on the aromatic ring as well as double bonds were tolerated under the catalytic conditions (Table 10). Moreover, sterically challenging substrates were hydrogenated in very high enantioselectivities. In the case of diketones, the corresponding dialcohols were obtained with high ee values (up to 97%), albeit in moderate diastereoselectivities. Interestingly, it was found that, with an increase in steric bulk at the alkyl chain of the aryl alkyl ketones, the enantioselectivities of the resulting alcohols increased significantly.

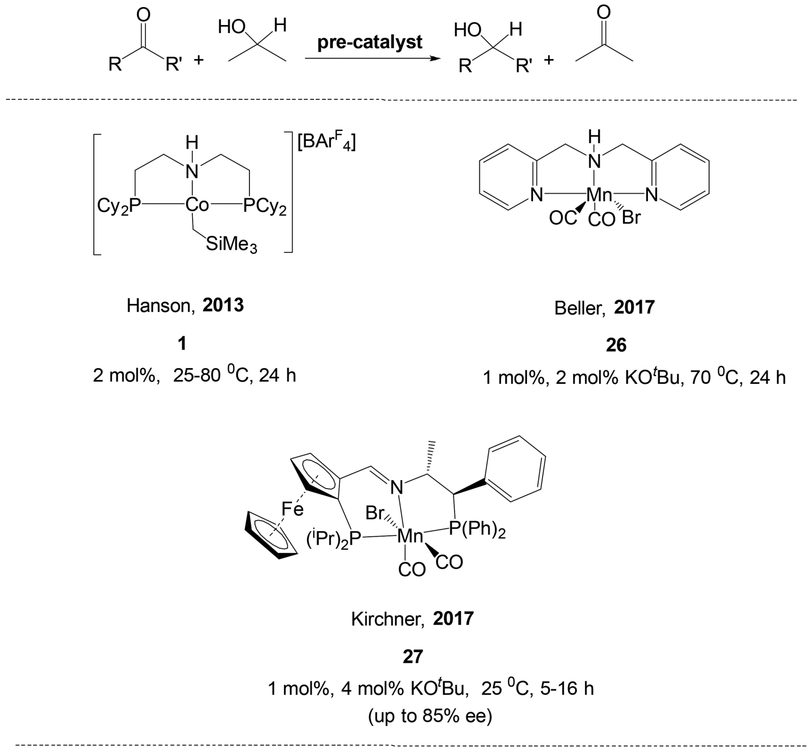
Soon after this report, Beller and co-workers[79] reported a similar transformation using the chiral manganese complex **25** under mild conditions (30−40 °C and 4 h) using 30 bar of H_2 pressure (Scheme 23). Aliphatic ketones are hydrogenated with high enantioselectivity, higher than that for aromatic ketones. The authors proposed[71] that the reaction proceeds via an outer-sphere hydrogenation[80] mechanism. Under the catalytic conditions enantiomerically enriched alcohols were obtained in up to 84% ee.

3.2. Transfer Hydrogenation of Ketones.

Transfer hydrogenation, the formal addition of hydrogen to an unsaturated molecule from a source other than gaseous H_2, is a safe and operationally simple alternative to the classical hydrogenation route.

Zhang and Hanson[81] reported a cobalt-based catalyst for achiral transfer hydrogenation of ketones catalyzed by **1** (Scheme 24). The reaction works well for a number of carbonyl

Scheme 24. Transfer Hydrogenation of Ketones Catalyzed by Co and Mn Complexes



Hanson, **2013**

1

2 mol%, 25-80 ^{0}C, 24 h

Beller, **2017**

26

1 mol%, 2 mol% KO^{t}Bu, 70 ^{0}C, 24 h

Kirchner, **2017**

27

1 mol%, 4 mol% KO^{t}Bu, 25 ^{0}C, 5-16 h
(up to 85% ee)

compounds and produces the corresponding alcohols in up to 99% yield. Lemaire and co-workers[82] also reported the asymmetric transfer hydrogenation of ketones using cobalt complexes.

Furthermore, Beller and co-workers[83] reported the easily accessible manganese NNN pincer complex **26** for the transfer hydrogenation of a broad range of ketones with good to excellent yields (Scheme 24). The reaction proceeded under mild reaction conditions and with low catalyst loading, and various functional groups were tolerated under the catalytic conditions. Soon after this, the Kirchner group[84] reported an asymmetric variant of the transfer hydrogenation using the chiral PNP-based manganese complex **27**, which demonstrated good catalytic activity and enantioselectivity (up to 86%).

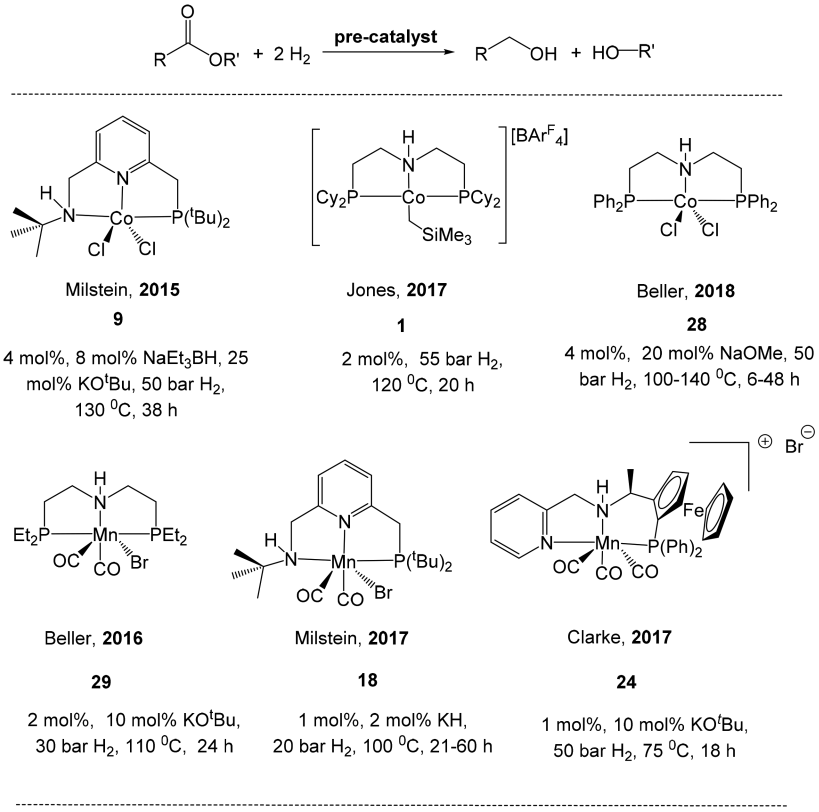
3.3. Hydrogenation of Esters. Hydrogenation of esters to alcohols is an important, industrially significant transformation in organic synthesis. Many alcohols, such as fatty alcohols, are commercially produced by the hydrogenation of fatty esters. In industry, this process is carried out using heterogeneous conditions with catalysts such as copper chromite under harsh conditions (200−300 atm of pressure, 200−300 °C temperature).[85] Using stoichiometric reduction reactions with hydride reagents, copious waste is generated. To overcome these drawbacks, in addition to low functional group tolerance, catalytic methods are receiving much attention. In 2006, Milstein reported[86] the first example of ester hydrogenation under low pressure (5 atm) using a dearomatized PNN Ru catalyst, and ester hydrogenation based on complexes of late transition metals have received much attention since then.[5c,d] In recent years the main focus has been diverted to the use of earth-abundant metals for similar transformations. Along this line, the Beller[87] and Milstein[9a] groups have demonstrated that iron pincer complexes can be used for ester hydrogenation with high catalytic activity.

The Milstein group[88] reported in 2015 the efficient hydrogenation of esters to the corresponding alcohols catalyzed by the cobalt precatalyst **9** (Scheme 25). Interestingly, the reaction requires enolizable esters and actually proceeds via C═C hydrogenation. The reaction works well in the presence of excess base (25 mol %), which helps to establish an ester−enolate equilibrium (Scheme 26). The enolate intermediate then undergoes hydrogenation to generate the salt of a hemiacetal intermediate which rearranges to generate an aldehyde and alkoxide, followed by the hydrogenation of the aldehyde to the corresponding alcohol and regeneration of the catalytic base.

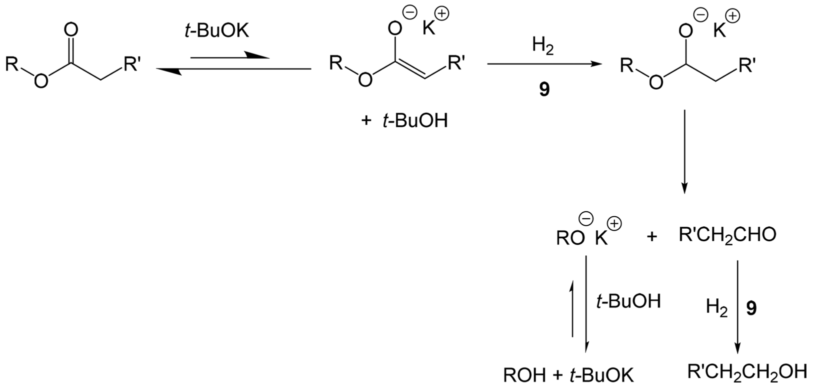
After this report, Jones and co-workers[89] reported the cobalt catalyst **1**, which hydrogenates both aromatic and aliphatic esters with good to excellent yields (up to 98%). Under the catalytic conditions the cyclic ester γ-valerolactone was hydrogenated to the corresponding diol in 91.6% isolated yield (Scheme 25). Very recently, Beller and co-workers[90] reported the cobalt complex **28**, which hydrogenates a wide range of aromatic, aliphatic, and cyclic esters very efficiently. In addition to this, in 2015 Elsevier, de Bruin, and co-workers[91] demonstrated that the cobalt catalyst generated in situ from triphos (tridentate phosphine, $CH_3C(CH_2PPh_2)_3$) and $Co(BF_4)_2{\cdot}6H_2O$ catalyzes the reduction of esters and carboxylates.

In addition to this, in 2016 Beller and co-workers[92] reported the first manganese-catalyzed hydrogenation of esters to alcohols by well-defined PNP manganese complex **29** (Scheme 25). Various esters, including electron-donating and -withdrawing substituents, as well as heterocyclic esters undergo the reduction process smoothly with good isolated yields of the alcohols (up to 98%) (Table 11). Interestingly, isolated double bonds survived under these reaction conditions, whereas conjugated examples were reduced. Similar to ketone hydrogenations catalyzed by the manganese complex **14**, an outer-sphere mechanism for the ester hydrogenations was proposed in this case. Initially, the deprotonation of **29** generates the similar catalytically active amido complex **29a**, which undergoes reversible

Scheme 25. Hydrogenation of Esters Catalyzed by Co and Mn Complexes



Scheme 26. Plausible Mechanism of Ester Hydrogenation Catalyzed by Co Complex 9



H_2 addition to form **29b** (Scheme 27). As shown in Scheme 27, the ester is reduced to an alcohol in two cycles: first to an aldehyde via a hemiacetal and then to the alcohol. Notably, it was observed that an increase in the bulk of the ligand resulted in a decrease in the catalytic activity of the resulting manganese complex.

Recently, Milstein and co-workers[93] have demonstrated independently that the PNN(H)-pincer-ligated manganese complex **18** (Scheme 25) can be applied to the hydrogenations of esters (Scheme 25). The reaction proceeded with the generation of the corresponding amido complex [Mn(PNN)$(CO)_2$] upon treatment with the base. The resulting amido complex reversibly activates H_2 to form the corresponding monohydride complex [Mn(PNNH)$(CO)_2$(H)]. Subsequently, the monohydride complex transforms the ester to the corresponding alcohol. This environmentally benign reaction proceeded under mild conditions (100 °C, 20 bar) with a broad substrate scope (Table 11).

The chiral PNN manganese complex **24** (Scheme 25) reported by Clarke and co-workers, used for the asymmetric hydrogenations of ketones, was also a highly active catalyst for the hydrogenations of esters under relatively mild conditions (1 mol % **24**, 50 bar H_2, 75 °C).[78] Both aryl and alkyl carboxylic esters were hydrogenated in high yields (up to 99%). Furthermore, Pidko and co-workers[94] very recently reported the catalytic hydrogenation of esters by using a new non-pincer-type manganese complex based on bidentate aminophosphine ligands.

3.4. Hydrogenation of Nitriles. The catalytic hydrogenation of nitriles to primary amines represents an atom-efficient and environmentally benign methodology in organic chemistry. However, this reaction is challenging, as it often displays crucial selectivity problems, forming imines and a mixture of primary, secondary, and tertiary amines.[95]

In 2015, Milstein and co-workers[96] reported the first homogeneous cobalt catalyzed hydrogenation of nitriles to primary

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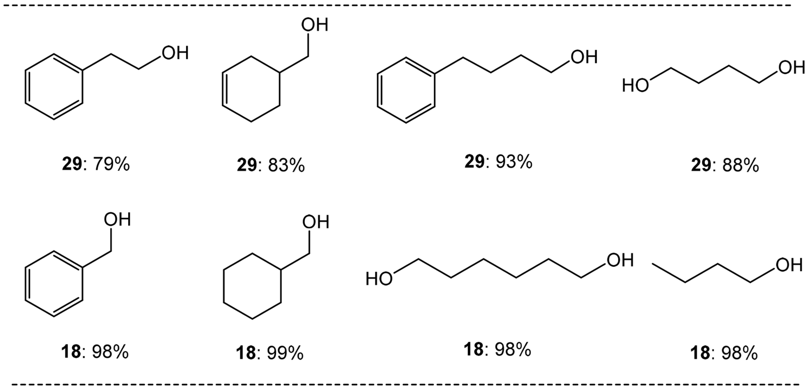
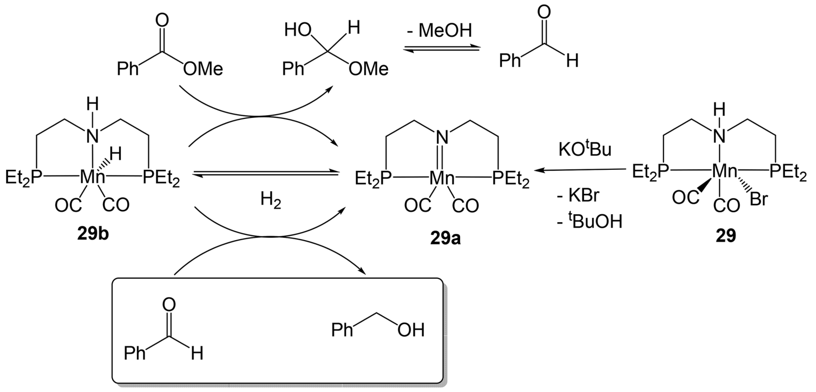
ACS Catal. 2018, 8, 11435−11469

Table 11. Selected Examples of Hydrogenation Products of Esters Catalyzed by 29[a] and 18[b]

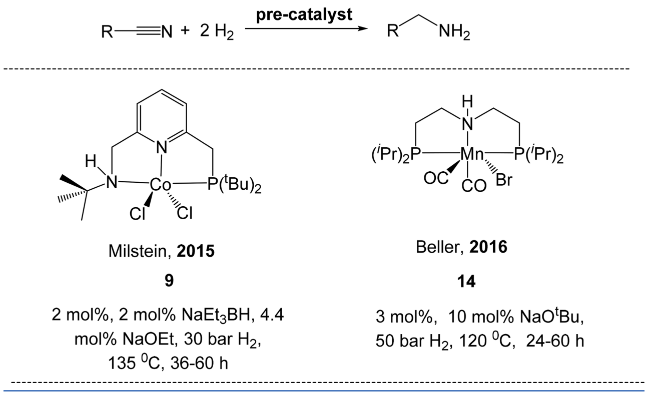


[a]Reaction conditions: substrate (1 mmol), **29** (2 mol %), KOtBu (10 mol %), H_2 (30 bar), 110 °C, 24 h. [b]Reaction conditions: substrate (1 mmol), **18** (1 mol %), KH (2 mol %), H_2 (20 bar), 100 °C, 21−60 h.

Scheme 27. Mechanism of Ester Hydrogenation Catalyzed by Manganese Complex 29



Scheme 28. Hydrogenation of Nitriles Catalyzed by Co and Mn Complexes



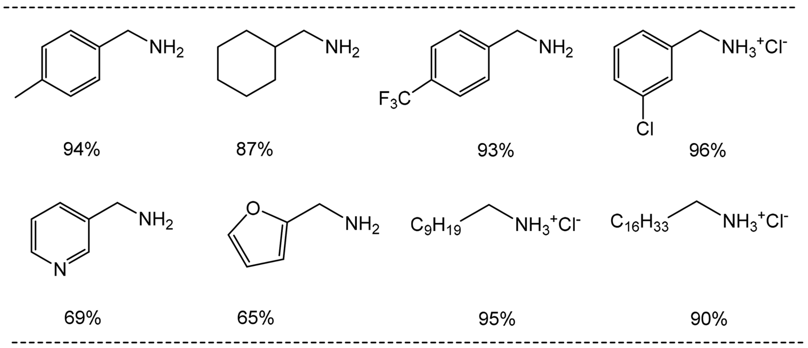
amines (Scheme 28). The precatalyst **9** exhibited a broad substrate scope, hydrogenating a number of (hetero)aromatic and aliphatic nitriles to the corresponding primary amines. Both electron-donating and electron-withdrawing functional groups survived under the relatively mild catalytic conditions (30 bar H_2 pressure). Soon after this report, Zhou, Liu, and co-workers[97] reported the transfer hydrogenation of nitriles to the corresponding primary, secondary, and tertiary amines in the presence of cobalt pincer complex using ammonia borane as a hydrogen source. Under the catalytic conditions, the catalyst demonstrated >2000 TONs (turnover numbers) for the transfer hydrogenation of nitriles.

Recently, Beller and co-workers[98] reported the first manganese-catalyzed hydrogenation of nitriles to amines (Scheme 28). The reaction proceeds under 50 bar of H_2 pressure with 3 mol % of precatalyst (**14**) loading (Table 12). Under the optimized condition, nitriles bearing electron-donating and electron-withdrawing groups, as well as heterocyclic aromatic and aliphatic nitriles, were converted to the primary amine in high yields (up to 99%).

3.5. Hydrogenation of Amides. In 2017, Beller and co-workers[99] demonstrated the reduction of amides to alcohols and amines by using the imidazole-based precatalyst **30** (Scheme 29). The air-stable complex **30** was synthesized by the reaction of the corresponding ligand with $[MnBr(CO)_5]$ in EtOH at 90 °C. The manganese complex **30** exhibited high catalytic activity under 30 bar of H_2 at 100 °C, in the presence of base, resulting in hydrogenation of a wide range of amides to the corresponding alcohols and amines. Under the optimized catalytic conditions, activated and nonactivated secondary and tertiary amides and the more challenging primary amides were hydrogenated in high yields. Interestingly, it was observed that, in the absence of the external base, the activity of the manganese catalyst was completely shut down, suggesting the formation of an amido complex as an active catalyst. This mechanism of the amide hydrogenation is similar to that proposed earlier for ester hydrogenation (Scheme 27). Moreover, formamides and more challenging primary amides were also hydrogenated and the catalyst showed very high selectivity for the amide reduction over carbamates and ureas.

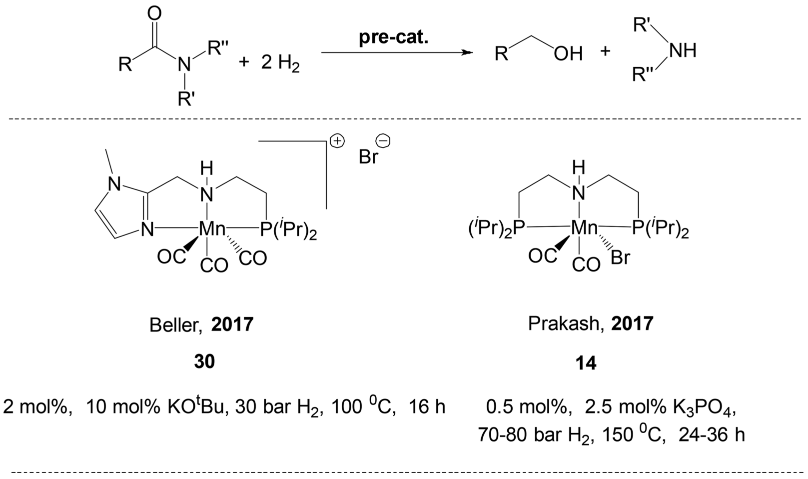
Soon after this report, Prakash and co-workers[100] reported the manganese-catalyzed hydrogenation of formamides, synthesized in situ from CO_2, H_2, and amine, using complex **14**.

Table 12. Selected Examples of Hydrogenation of Nitriles Catalyzed by 14[a]



[a]Reaction conditions: substrate (1 mmol), **14** (3 mol %), NaOtBu (10 mol %), H_2 (50 bar), 120 °C, 24−60 h.

Scheme 29. Hydrogenation of Amides Catalyzed by Mn Complexes



3.6. Hydrogenation of Olefins. Budzelaar and co-workers[101] showed that bis(imino)pyridine cobalt dichloride (activated with excess Al^iBu_3), or the corresponding alkyl complexes, is effective for the hydrogenation of 1- and 2-alkenes. Detailed spectroscopic and computational studies supported the formation of a Co−H bond followed by olefin insertion and σ-bond metathesis of the metal alkyl with H_2. However, the substrate scope in this report is quite limited. In 2012 and 2013, Hanson and co-workers reported the PNP cobalt alkyl complexes **1** and **31**, which efficiently catalyze the hydrogenation of a number of alkenes (Scheme 30).[71,102] The reactions proceed under very mild conditions (25 °C) with 1 atm of H_2 pressure in both cases. A number of internal and terminal alkenes were hydrogenated to the corresponding alkanes in quantitative yield. In addition to these reports, the Fout group[103] reported the Co^I−N_2 precursor **32**, supported by a monoanionic pincer bis(carbene) ligand, for the hydrogenation of alkenes. A detailed experimental study suggests that a Co(I)/Co(III) redox process is involved in the olefin hydrogenation process (Scheme 30).

Furthermore, Chirik and co-workers[104] reported the asymmetric hydrogenation of substituted styrenes using a bis(imino)pyridine cobalt alkyl complex (Scheme 31). The reaction proceeds under 4 atm of H_2 pressure with 5 mol % of catalyst loading at 22 °C. Hydrogenation of phenylated alkenes resulted in enantiomeric excesses of 80−98% (Table 13). Notably, more sterically crowded olefins produced higher selectivity, albeit with reduced activity. The same group also reported a detailed mechanistic study of the cobalt-catalyzed asymmetric hydrogenation of alkenes.[105] Moreover, analysis of the stereochemical outcome of the hydrogenated products, coupled with isotopic labeling, stoichiometric, and kinetic studies, established that 1,2-alkene insertion was both a turnover-limiting and enantio-determining step. Moreover, no evidence for erosion of the cobalt alkyl stereochemistry by competing β-hydrogen elimination processes was observed under the catalytic conditions.

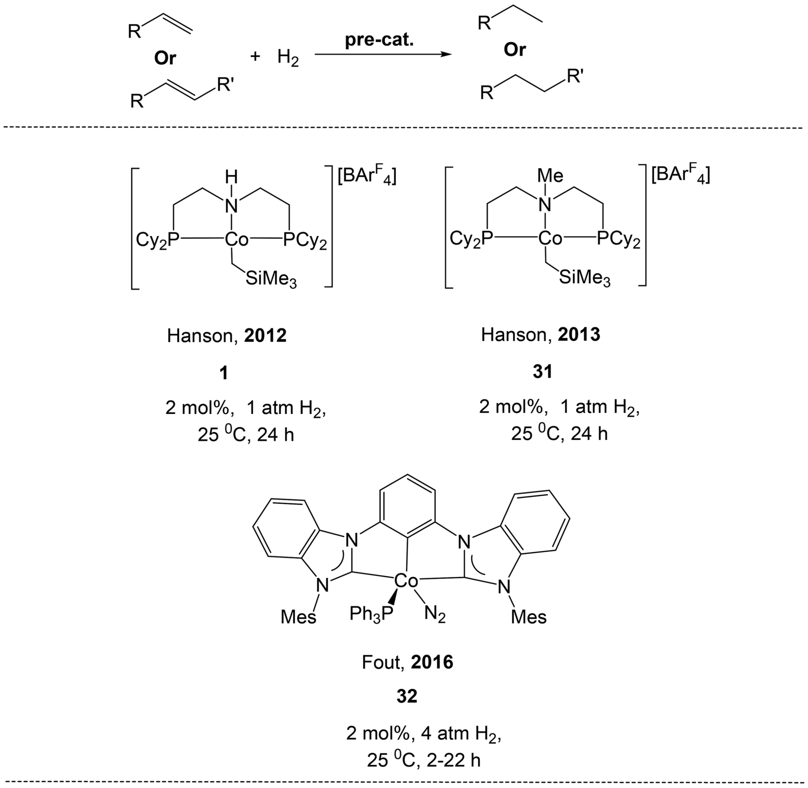
In addition to this, Chirik and co-workers[106] also reported cobalt precursors for high-throughput discovery of asymmetric alkene hydrogenation using a bisphosphine ligand at room temperature.

Furthermore, Zhang and co-workers[107] reported the cobalt-catalyzed transfer hydrogenation of alkenes. A range of olefins including aromatic and aliphatic alkenes as well as internal and cyclic alkenes were transfer-hydrogenated in good to excellent yields (up to 99%). The catalyst also exhibited good functional group and water tolerance in olefin transfer hydrogenation reactions.

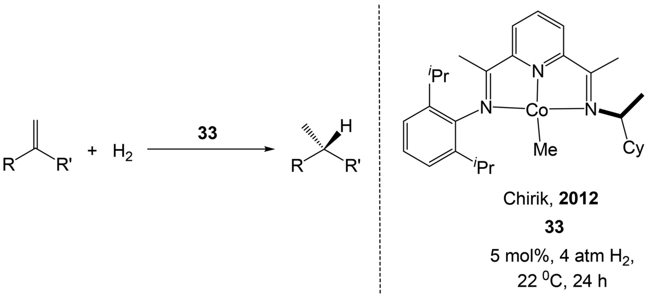
3.7. Hydrogenation of Imines. Hanson and co-workers[71] reported a cobalt(II) alkyl precatalyst for hydrogenation of imines to the corresponding secondary amines in good yield. The hydrogenation reaction was carried out under 4 atm of H_2 pressure at 60 °C using 2 mol % of precatalyst loading.

3.8. Hydrogenation of Carbon Dioxide. Transformation of CO_2 to value-added products is a subject of much current research interest, since it provides an abundant and inexpensive carbon source. Among the various possible transformations, the catalytic hydrogenation of CO_2 to methanol and to formic

Scheme 30. Hydrogenation of Alkenes Catalyzed by Co Complexes



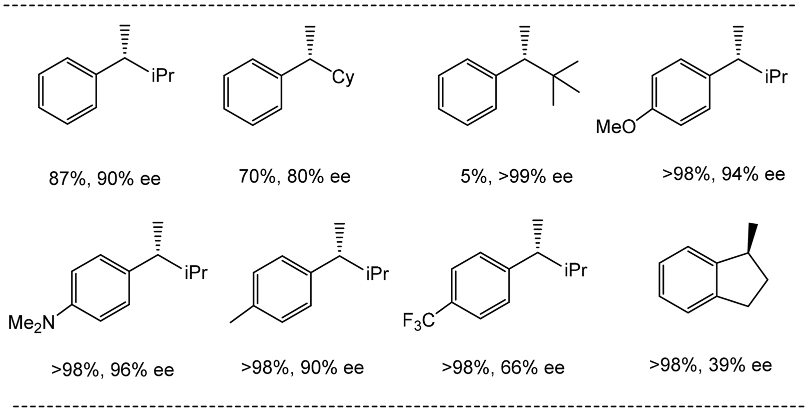
Scheme 31. Asymmetric Hydrogenation of Alkenes Catalyzed by Co Complex 33



acid (FA) and its derivatives is a subject of increasing interest. FA is a widely employed commodity chemical and can be used as a hydrogen storage material.

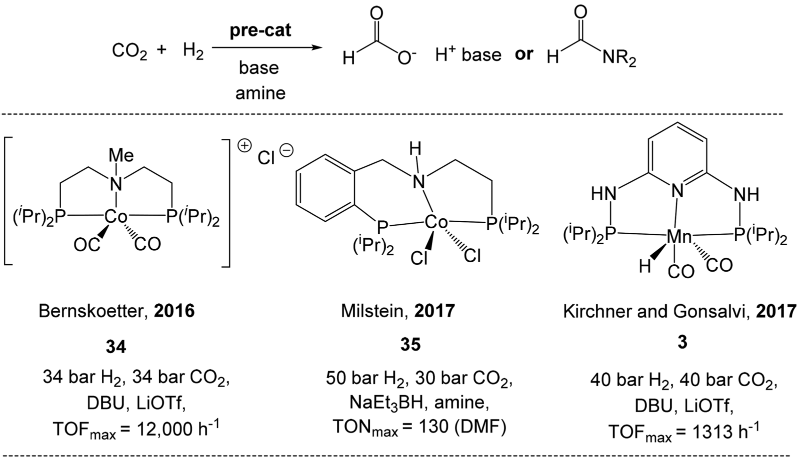
Beller and co-workers[108] reported a highly efficient cobalt catalyst system, generated in situ from Tetraphos (PP_3:$P(CH_2CH_2PPh_2)_3$) and $Co(BF_4)_2 \cdot 6H_2O$, for the reduction of CO_2 to formate and formamides. Similarly, Muckerman, Himeda, Fujita, and co-workers[109] developed a cobalt complex based on proton-responsive ligands for the reduction of CO_2 in aqueous media. Linehan and co-workers[110] demonstrated a highly active cobalt complex based on the bis(dimethylphosphino)ethane ligand, which operates under mild conditions in the presence of Verkade's base. Moreover, Bernskoetter and co-workers[111] showed that the cobalt complex **34**, based on the pincer ligand $MeN[CH_2CH_2(P^iPr_2)]_2$, exhibited CO_2 hydrogenation catalysis (Scheme 32). Interestingly, better TONs were achieved when **34** was used in combination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base and LiOTf as Lewis acid.

Table 13. Selected Examples of Asymmetric Hydrogenation of *gem*-Disubstituted Alkenes Catalyzed by 33[a]



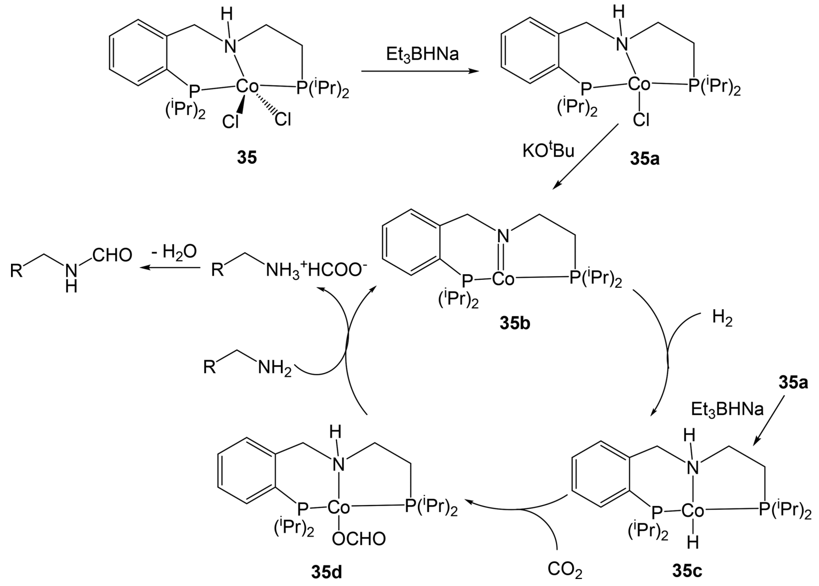
[a] Reaction conditions: **33** (5 mol %), KOtBu (10 mol %), H_2 (4 atm), 22 °C, 24 h.

Scheme 32. Hydrogenation of CO_2 to Formates or Formamides Using Co and Mn Catalysts[a]



[a]Abbreviations: TOF = turnover frequency, TON = turnover number, OTf = trifluoromethanesulfonate; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

Scheme 33. Proposed Mechanism for the N-formylation of Amines using CO_2 and H_2 Catalyzed by 35



Furthermore, Milstein and co-workers[112] recently reported a well-defined cobalt complex **35** for the hydrogenation of CO_2 with amines (Scheme 32). Under the optimized conditions, the reaction works well for both primary (aliphatic and aromatic) and secondary amines, providing good to excellent yields of formamides (up to 99%) under relatively mild CO_2 and H_2 pressures (30 bar each). Mechanistically, treatment of PPN(H)-$Co^{II}Cl_2$ (**35**) with 1 equiv of $NaEt_3BH$ resulted in PPN(H)-$Co^{I}Cl$ (**35a**). It is proposed that reaction of **35a** with KO^{t}Bu results in the formation of the coordinatively unsaturated intermediate **35b** (Scheme 33). This intermediate generates under H_2 pressure the Co(I) hydride intermediate **35c**. Reaction of CO_2 with **35c** results in formation of the η^1-formato intermediate **35d**, with insertion of CO_2 into the Co−H bond. The intermediate **35d** reacts further with excess amine present in the reaction mixture to form the formate salt. Subsequently, the formate salt liberates water and regenerates the active catalyst **35b**. Recently, Yang and co-workers[113] provided a computational understanding of the cobalt-catalyzed hydrogenation of CO_2 to formic acid.

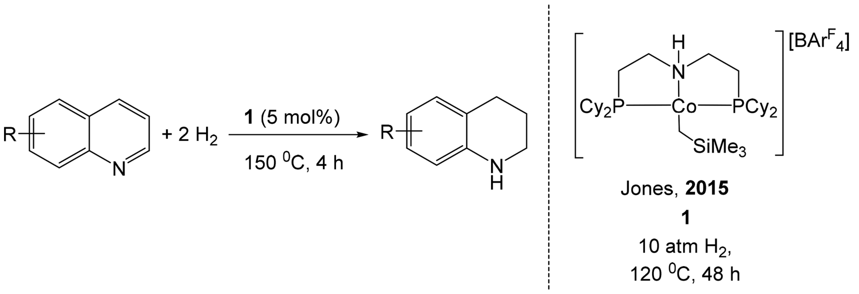
In 2017 Kirchner, Gonsalvi, and co-workers[114] reported the first Mn(I)-catalyzed hydrogenation of CO_2 to FA (Scheme 32). The manganese hydride catalyst **3** exhibited high stability and reactivity. A turnover number (TON) of 10000 was achieved after 24 h using 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) as the base at 80 °C and under 80 bar of CO_2 and H_2 pressure. Interestingly, addition of a Lewis acid (LiOTf) as a cocatalyst resulted in a drastic catalytic activity increase and very high TONs, greater than 30000, were achieved with very low catalyst loading (0.002%).

Furthermore, Prakash and co-workers[100] reported that the manganese complex **14** catalyzes the reduction of CO_2 with H_2 to methanol in the presence of amines via a formamide intermediate. Very recently, Nervi, Khusnutdinova, and co-workers[115] demonstrated that a manganese complex bearing a bidentate 6,6′-dihydroxy-2,2′-bipyridine ligand acts as an efficient catalyst for CO_2 hydrogenation to formate and formamide.

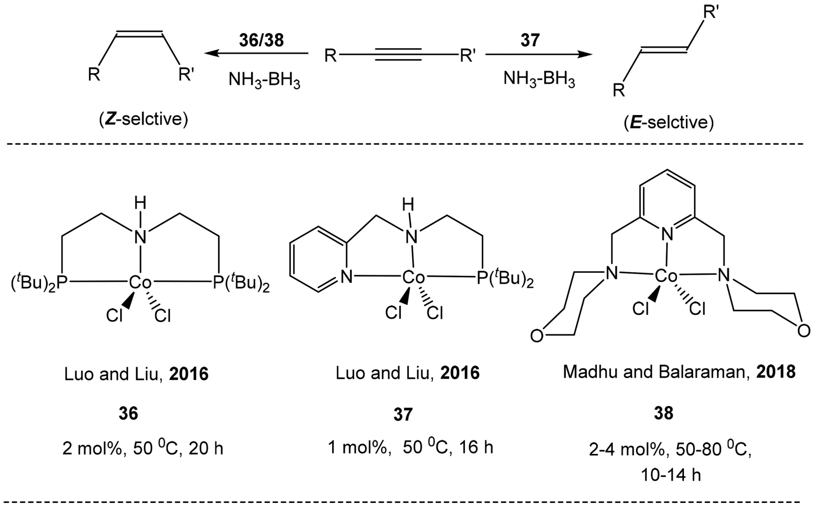
3.9. Hydrogenation of Unsaturated N-heterocycles.

Jones and co-workers[68] reported the hydrogenation of unsaturated N-heterocycles catalyzed by the cobalt pincer complex **1** (Scheme 34). Under the optimized conditions, hydrogenation

Scheme 34. Hydrogenation of Unsaturated Heterocycles Catalyzed by 1



Scheme 35. Semihydrogenation of Alkynes Catalyzed by the Co Complexes



of quinoline derivatives resulted in quantitative conversions to produce the respective hydrogenated products in 2 days. Notably, with all of these quinoline substrates, the aromatic phenyl ring remained intact after the reaction. Hydrogenation of 2,6-lutidine and 1,5-naphthyridine did not yield the corresponding hydrogenated product.

3.10. Transfer Semihydrogenation of Alkynes.

Luo, Liu, and co-workers[116] reported in 2016 the first example of cobalt-catalyzed transfer semihydrogenation of alkynes to form both (Z)-and (E)-alkenes (Scheme 35). A series of well-defined cobalt catalysts were used in the presence of ammonia−borane (AB) as the hydrogen source. The reaction proceeds under relatively mild conditions (25−50 °C) with low catalyst loading (1−2 mol %). Interestingly, when complex **36** was used as precatalyst, the (Z)-alkene was obtained selectively, while the (E)-alkene was formed when complex **37** was used. A number of internal and terminal alkynes having electron-donating and -withdrawing groups underwent the semihydrogenation reaction with good yields and selectivity in the absence of any additives. Notably, this cobalt-catalyzed reaction proceeds with high efficiency, and up to 460 turnovers were obtained.

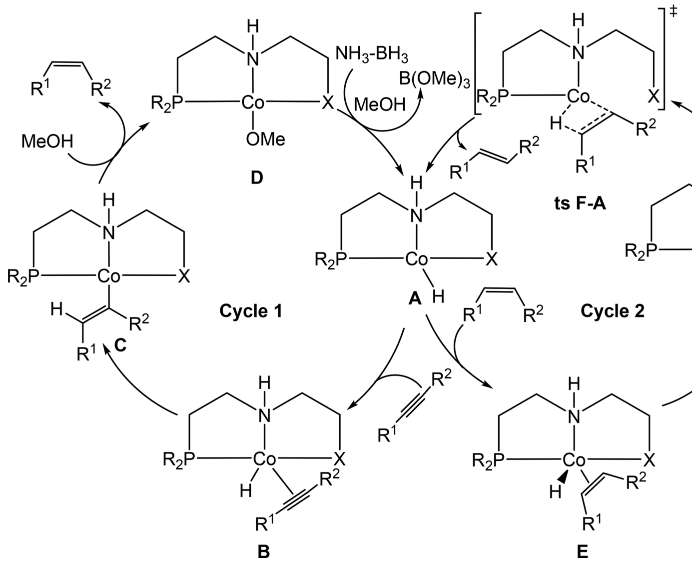
The mechanistic details for the semihydrogenation were probed experimentally, including deuterium labeling experiments (Scheme 36). It is proposed that, initially, the cobalt dichloride complexes **36** and **37** are reduced by AB to generate the catalytically active cobalt hydride complex **A**. Coordination of the alkyne to complex **A**, followed by the insertion of the alkyne into the Co−H bond, leads to formation of the alkenyl cobalt complex **C**. Subsequently, protonation of the Co−C bond by methanol affords the (Z)-alkene intermediate and the methoxy cobalt complex **D**. Intermediate **D** further reacts with AB to regenerate complex **A** along with the production of $B(OMe)_3$. The Z/E alkene isomerization process would then be accomplished by the next catalytic cycle (cycle 2). The insertion of the (Z)-alkene intermediate into the Co−H bond, followed by a β-hydride elimination, finally leads to the generation of the thermodynamically more stable (E)-alkene product. The isomerization process is promoted by the less steric hindered cobalt complexes **37** and leads to the formation of (E)-alkene products. In contrast, the bulky cobalt catalyst **36** effectively prevents this isomerization process and affords the (Z)-alkene products.

Very recently, Madhu, Balaraman, and co-workers[117] reported the NNN-based cobalt pincer precatalyst **38** for the semihydrogenation of alkynes to selectively produce (Z)-alkenes (Scheme 35). AB was used in this study as a bench-stable hydrogen source.

4. FORMATION OF AMMONIA FROM DINITROGEN

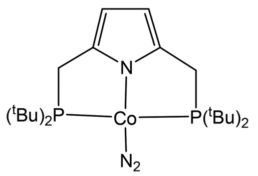
In 1983, Yamamoto and co-workers[118] reported the first example of a cobalt dinitrogen complex, $[Co(H)(N_2)(PPh_3)_3]$, synthesized directly using dinitrogen gas. Treatment of this complex with $MgEt_2$, nBuLi, or metallic sodium in THF led to the formation of the bimetallic/trimetallic dinitrogen-bridged species $[Co(N_2)(PPh_3)_3]_2Mg(THF)_4$, $[Co(N_2)(PPh_3)_3]Li(THF)_3$, and $[Co(N_2)(PPh_3)_3]Na(THF)_3$. Subsequently, protonation with HCl or H_2SO_4 led to the formation of hydrazine and ammonia. After this report, several detailed studies on the stoichiometric reactivity of a variety of cobalt dinitrogen

Scheme 36. Plausible Mechanism for the Transfer Hydrogenation of Alkynes



Scheme 37. Catalytic Reduction of Dinitrogen by Co Complex 39

$$N_2 + KC_8 + [H(OEt_2)_2]BAr^F{}_4 \xrightarrow{\textbf{39}} NH_3 + NH_2NH_2$$



Yoshizawa and Nishibayashi, **2016**

39

1 atm N_2, 200 equiv. KC_8, 184 equiv. $[H(OEt_2)_2]BAr^F{}_4$, -78 ^{0}C, 1 h

complexes and the formation ammonia were carried out by several research groups.[119]

Yoshizawa, Nishibayashi, and co-workers[120] reported the direct formation of ammonia from molecular dinitrogen under mild reaction conditions using a cobalt dinitrogen complex bearing an anionic PNP-type pincer ligand (Scheme 37). Interestingly, it was observed that when complex **39** was employed as the catalyst in combination with excess of KC_8 as reductant and $[H(OEt_2)_2]BAr^F{}_4$ as proton source, the yield of nitrogenous products dramatically increased. The use of 200 equiv of KC_8 and 184 equiv of $[H(OEt_2)_2]BAr^F{}_4$ gave the largest amounts of ammonia and hydrazine (15.9 and 1.0 equiv, respectively, based on the catalyst). These results indicate that the cobalt dinitrogen complex bearing an anionic PNP-type pincer ligand can catalyze the conversion of molecular dinitrogen into ammonia and hydrazine, and up to 17.9 equiv of nitrogen atoms was fixed on the basis of the amount of catalyst used. Recently, the same group further extended[121] the nitrogen fixation reaction using iron and cobalt dinitrogen complexes with PSiP-type pincer ligands.

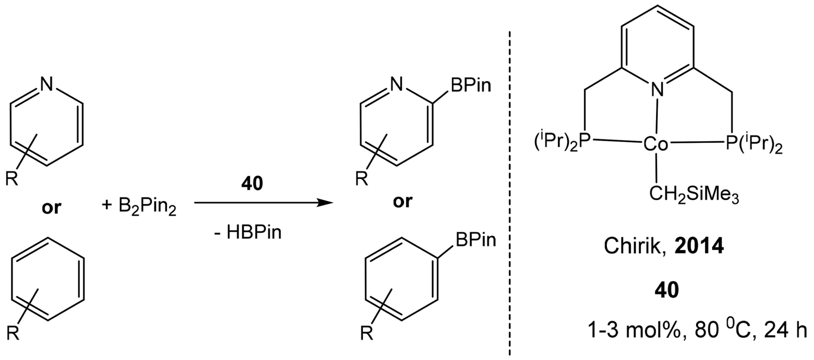
5. C–H BORYLATION REACTION

The selective functionalization of carbon–hydrogen bonds using homogeneous catalysts is a field of great interest.[122] Among the several methods developed for this transformation, metal-catalyzed borylation of arene $C(sp^2)$–H bonds is one of the most powerful tools due to orthogonal selectivity to traditional electrophilic aromatic substitution and the synthetic versatility of the resulting arylboronate products.[123]

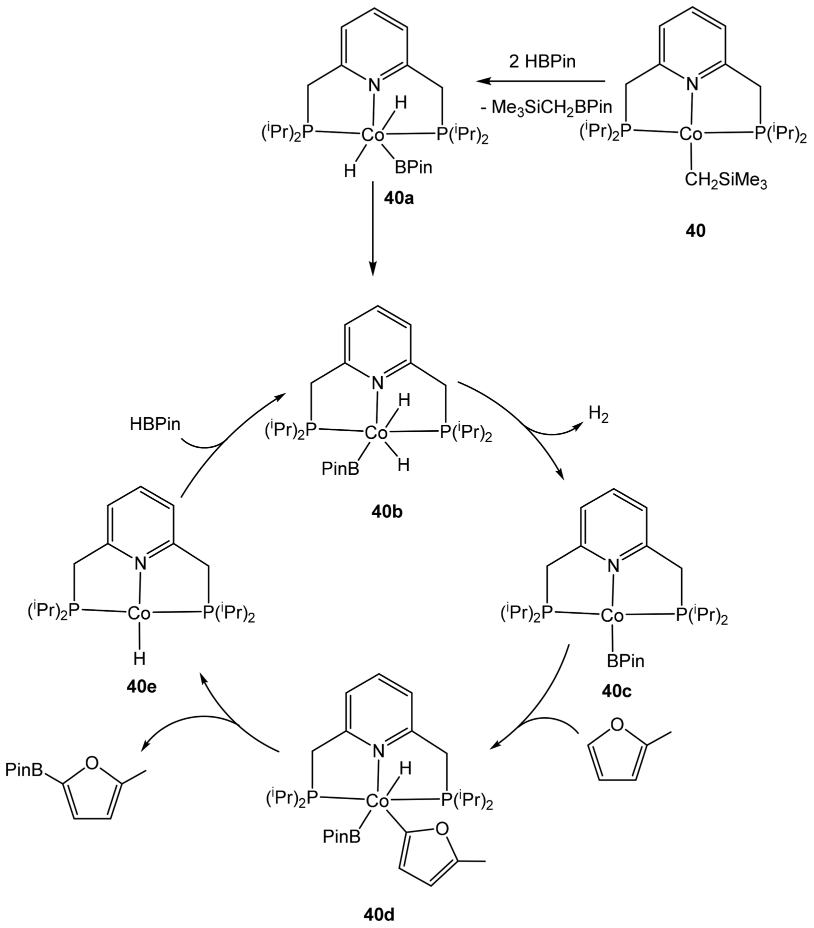
Chirik and co-workers[124] reported the cobalt-catalyzed C–H borylation reaction of heterocycles and arenes (Scheme 38). A number of cobalt(I) complexes based on NNN and PNP pincer ligands were tested for this study, and their catalytic activity was evaluated. The cobalt catalyst **40** operated under mild conditions (23–80 °C) with high activity and low catalyst loading (0.02–3 mol %). Notably, excess borane reagents were not required and up to 5000 turnovers of methyl furan-2-carboxylate were observed at ambient temperature using 0.02 mol % catalyst loadings.

A catalytic cycle that relies on a cobalt(I)–cobalt(III) redox couple was proposed for this reaction (Scheme 39). Initially, treatment of the cobalt complex **40** with 2 equiv of pinacolborane (HBPin) results in loss of 1 equiv of Me_3SiCH_2BPin with concomitant formation of the new cobalt species $(PNP)CoH_2(BPin)$ (**40a**,**b**). The identity of this Co(III) oxidative addition product was confirmed by X-ray diffraction analysis and NMR spectroscopy. Subsequently, **40b** (cis isomer) undergoes reductive elimination of H_2 either by isomerization to the cis isomer or by dissociation of a phosphine ligand, thus generating the Co^I-BPin complex. Following H_2 elimination, the resulting cobalt(I) boryl complex, (PNP)CoBPin (**40c**), undergoes oxidative addition of a C–H bond of the substrate. Reductive elimination of the B–C bond furnishes the C–H borylated product, and oxidative addition of HBPin regenerates *cis*-$(PNP)CoH_2(BPin)$ (**40b**). The same group extended

Scheme 38. C−H Borylation of (Hetero)arenes Catalyzed by Co Complex



Scheme 39. Mechanism of C−H Borylation Reaction Catalyzed by Cobalt Complex 40



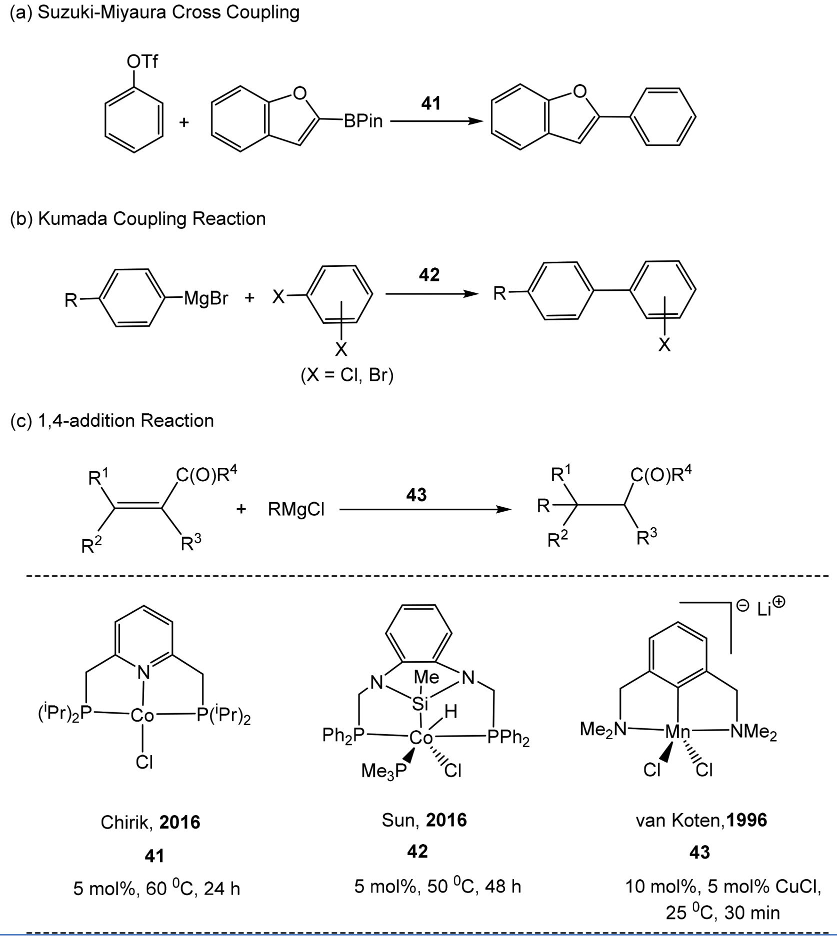
the C−H borylation reaction to substituted arenes using air-stable cobalt pincer systems.[125] Recently, Cui and co-workers reported the cobalt-catalyzed regioselective borylation of arenes bearing a bis(N-heterocyclic silylene)pyridine pincer ligand.[126]

6. CARBON−CARBON BOND FORMATION REACTIONS

Chirik and co-workers[127] reported the cobalt-pincer catalyzed Suzuki−Miyaura cross coupling between aryl triflates and heteroaryl boron nucleophiles. The reaction proceeds under relatively mild conditions (60 °C) in a basic medium with 5 mol % of precatalyst (**41**) (Scheme 40). A mechanistic study established that the reaction involves formation of tetrahedral, high-spin bis(phosphino)pyridine cobalt(I) alkoxide and aryloxide complexes. Notably, under the catalytic conditions cobalt compounds bearing small alkoxide substituents underwent swift transmetalation at 23 °C and proved to be kinetically unstable toward β-H elimination. For secondary alkoxides, balanced stability and reactivity was observed under the optimized conditions. Moreover, transmetalation reactivity was proposed for the coupling reaction using **41**. Similarly, Bhat and co-workers[128] also reported the Suzuki−Miyaura cross-coupling reaction using a cobalt pincer complex.

Sun and co-workers[129] reported a N-heterocyclic-based PSiP pincer cobalt complex for Kumada coupling reactions (Scheme 40). The catalytically active cobalt(III)-hydride complex **42** was synthesized by treatment of $HSiMe(NCH_2PPh_2)_2C_6H_4$

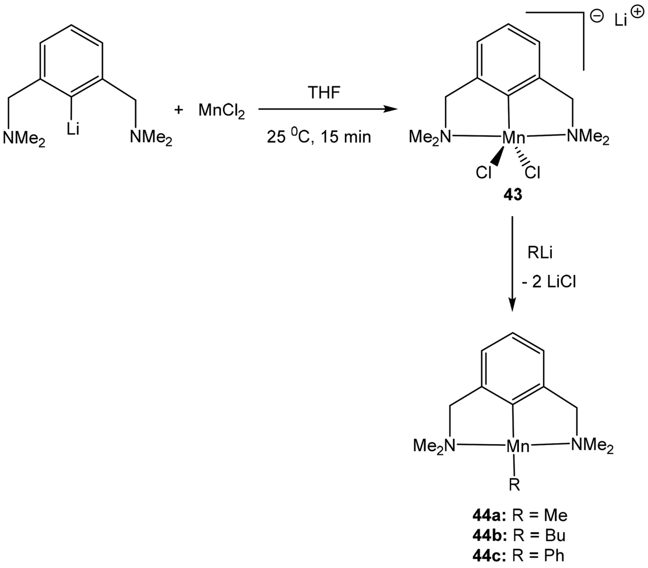
Scheme 40. C−C Bond Formation Reaction Catalyzed by Cobalt and Manganese Complexes



with $CoCl(PMe_3)_3$ or the combination of complex $Co(PMe_3)_2$-$(SiMe(NCH_2PPh_2)_2C_6H_4)$ with HCl. With a catalyst loading of 5 mol %, complex **42** displayed efficient catalytic activity for Kumada cross-coupling reactions of aryl chlorides and aryl bromides with Grignard reagents. The same group also reported[130] the Kumada cross-coupling using a N-heterocyclic silylene (NHSi) cobalt hydride complex.

In 1996, van Koten and co-workers[131] demonstrated the manganese-catalyzed C−C bond-formation reaction. The Mn(II) complex **43** was synthesized by a single step upon treatment with the Li salt of the NCN pincer ligand with $MnCl_2$ (Scheme 41). Complex **43** exhibited catalytic activity in coupling reactions of Grignard reagents and organic bromides, as well as 1,4-addition reactions of Grignard reagents to *α*,*β*-unsaturated ketones in the presence of catalytic amounts of CuCl (Scheme 40). Apart from **43**, the diorganomanganese complexes **44a−c** were also isolated. These complexes as well as complex **43**, prepared in situ, exhibited similar reactivity. The authors suggested formation of a manganese−copper intermediate in the catalytic cycle. High chemoselectivity was achieved for the cross-coupled products, and excellent reactivity toward normally unreactive *β*,*β*-disubstituted ketones was observed in the 1,4-addition reaction.

Scheme 41. Synthesis of the Mn Complexes 43 and 44



7. MICHAEL ADDITION REACTION

Milstein and co-workers[132] have recently reported the Michael addition of nonactivated aliphatic nitriles catalyzed by the PNP-pincer manganese complex **2**. The preparation of this complex is shown in Scheme 42. Treatment of the cationic tricarbonyl complex with KO^tBu at room temperature yielded a mixture of the tricarbonyl complex **45** and the dicarbonyl complex **2** having a dearomatized ligand as backbone. Upon reflux in THF under argon, the mixture yielded the dicarbonyl complex **2**, which could be easily converted to **45** by treatment with CO. Complex **2** was characterized, isolated in 60% yield, and used for catalytic studies.

Scheme 42. Synthesis of Manganese Pincer Complexes 2 and 45

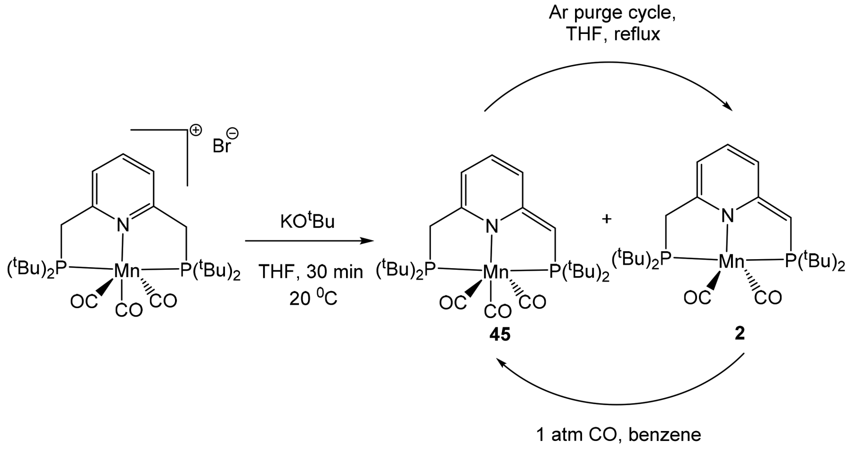
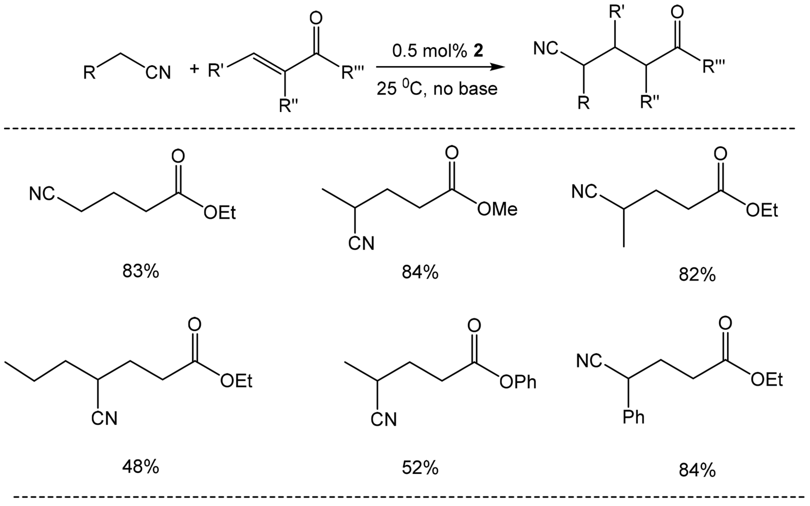


Table 14. Selected Examples of Michael Addition of Aliphatic Nitriles to *α*,*β*-Unsaturated Carbonyl Compounds Catalyzed by 2[a]



[a]Reaction conditions: substrate (2.5 mmol), **2** (0.5 mol %), 25 °C, 6−40 h.

Quite uniquely, the catalytic reactions between ethyl acrylate and a variety of unactivated aliphatic nitriles, which normally require high temperature and strong base, proceed smoothly at room temperature and in the absence of added base, using only 0.5 mol % of the manganese complex **2** (Table 14).[132] Additionally, various *α*,*β*-unsaturated carbonyl compounds reacted smoothly with propionitrile (Table 14). It was observed that the terminal substitution of the double bond had a strong influence on the conversion in the latter case. On the basis of intermediate isolation and DFT studies, it was shown that the reaction proceeds by a unique mechanism, which is based on generation of an enamido intermediate reversibly C−C bound to the ligand. Thus, the catalysis is mostly ligand based and is termed "template catalysis".

8. CYCLOADDITIONS OF ALKENES

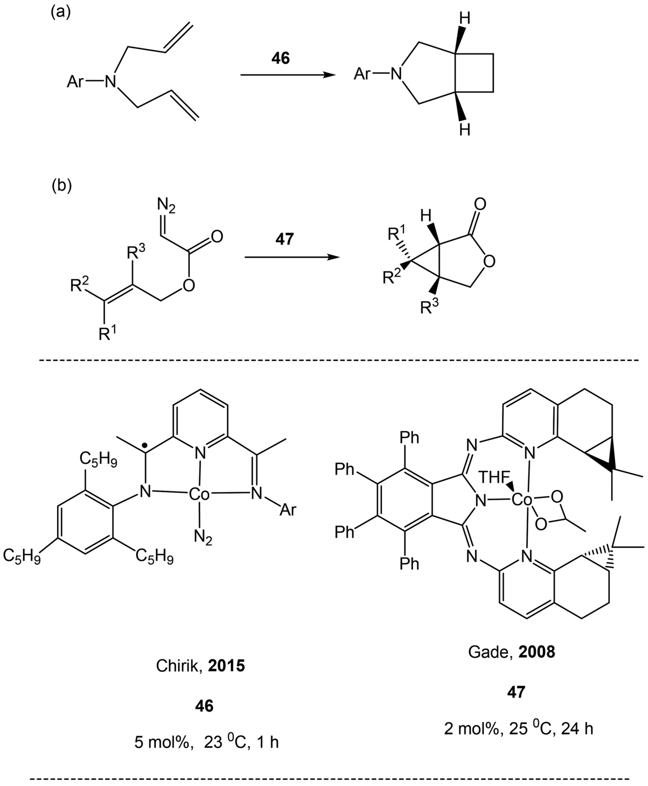
Chirik and co-workers[133] reported the pincer cobalt catalyzed [2*π* + 2*π*] cycloadditions of alkenes under mild conditions. In this study, the aryl-substituted bis(imino)pyridine cobalt dinitrogen complex **46** was found to be an effective catalyst for the intramolecular [2*π* + 2*π*] cycloaddition of *α*,*ω*-dienes to yield the corresponding bicyclic [3.2.0]heptane derivatives (Scheme 43). The reactions proceeded under mild conditions (23 °C) with unactivated alkenes, tolerating both amine and ether functional groups using 5 mol % catalyst loading.

Gade and co-workers[134] reported the chiral bis(pyridylimino)-isoindole based cobalt pincer complex **47** for asymmetric cyclopropanation (Scheme 43). The reaction works under mild reaction conditions (23 °C) with 2 mol % of catalyst loading. Both inter- and intramolecular asymmetric cyclopropanations result in high ee values of the resulting products (up to 93% ee).

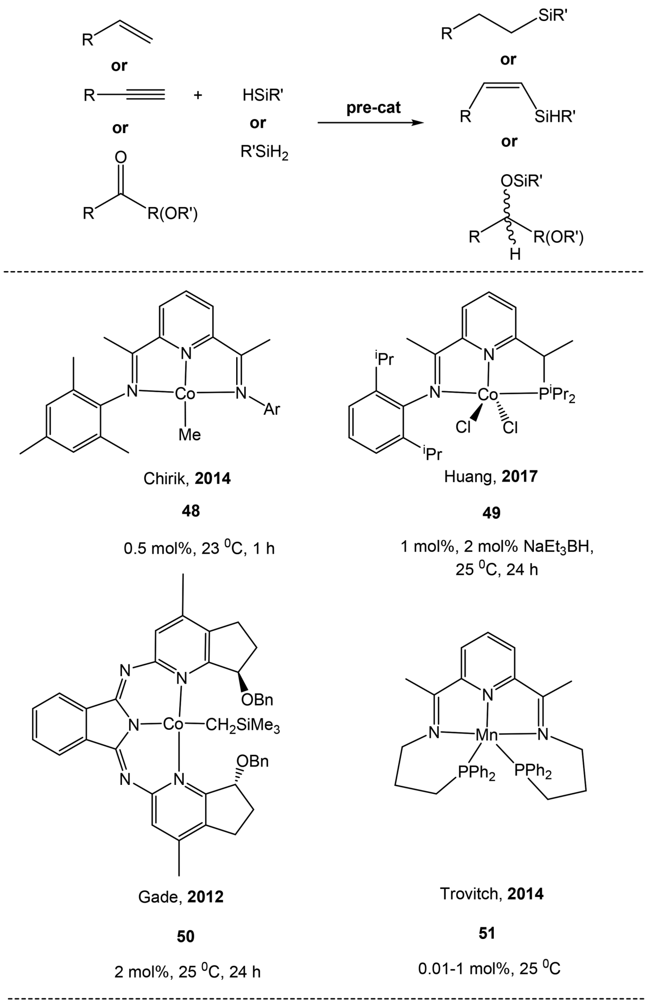
9. HYDROSILYLATION REACTION

Hydrosilylation of alkenes is an industrially significant reaction. In 2014, Chirik and co-workers[135] reported the dehydrogenative silylation of alkenes, catalyzed by the 2,6-iminopyridine-cobalt complex **48**. The reaction of $HSi(OSiMe_3)_2Me$ with 1-octyne (2 equiv) resulted in allylsilanes in more than 98% yield as a 3:1 *E*/*Z* mixture along with 1 equiv of *n*-octane. A detailed substrate scope study using 0.5 mol % of **48** as catalyst indicated the applicability of the catalytic system to a broad range of hydrosilanes ($HSi(OSiMe_3)_2Me$, $HSi(OEt)_3$, $HSiEt_3$, H_2SiPh_2, H_3SiPh) and linear terminal alkenes. Notably, the outcome of the cobalt-catalyzed dehydrogenative silylation reaction is substrate dependent, as the majority of the alkenes used in the study were converted to allylsilanes, whereas the reactions of 3,3-dimethylbutene and isobutene generated

Scheme 43. Cycloaddition Reaction Catalyzed by Cobalt Complexes



Scheme 44. Dehydrogenative Silylation Reaction Catalyzed by Cobalt and Manganese Complexes



vinylsilanes as the major products. The same group also reported the cobalt-catalyzed hydrosilylation of carbon dioxide using primary silanes and alkene hydrosilylation[136] with tertiary silanes.[137] Very recently, Huang and co-workers[138] demonstrated the cobalt-catalyzed (**49**) regio- and stereoselective hydrosilylation of terminal alkynes with Ph_2SiH_2 to generate (*Z*)-*β*-vinylsilanes with high functional group tolerance (Scheme 44). On the other hand, Li and co-workers[139] reported the hydrosilylation of carbonyl compounds catalyzed by a Co(III) hydride complex based on a CNC pincer ligand.

In addition, Gade and co-workers[140] reported the chiral tridentate monoanionic NNN-pincer cobalt alkyl complex (**50**) for the asymmetric hydrosilylation reaction of aryl alkyl ketones with a tertiary silane (Scheme 44). Moreover, recently Lu and co-workers[141] have reported highly enantioselective cobalt-catalyzed hydrosilylation of alkenes and alkynes to the corresponding silanes.

Trovitch and co-workers[142] reported the first manganese-based pincer catalyst that displays high activity in the hydrosilylation of ketones and esters (Scheme 44). The Mn(II) complex was prepared by starting from a bis(imino)pyridine pincer ligand and $MnCl_2$, followed by reduction with an excess of Na/Hg to give the formally zerovalent pentadentate manganese complex **51**. Complex **51** was a highly active precatalyst for the hydrosilylation of ketones, exhibiting TOFs of up to 76800 h^{-1} in the absence of solvent. Even with low catalyst loading (0.01 mol %), quaternary silane products were obtained efficiently. Under the catalytic conditions, Ph_2SiH_2 showed 26% conversion of the ketone, whereas no reaction was observed with Ph_3SiH or Et_3SiH. Additionally, acetophenone was completely and rapidly converted in the presence of 1 mol % of **51** using $PhSiH_3$, yielding a mixture of the corresponding di- and trisubstituted silyl ethers PhSiH[OCH(Me)(Ph)]$_2$ and PhSi[OCH(Me)(Ph)]$_3$. Moreover, it was observed that using various substituents at the para position of acetophenone also resulted in high yields, although extended reaction time was required, irrespective of the nature of the substituents (Table 15).

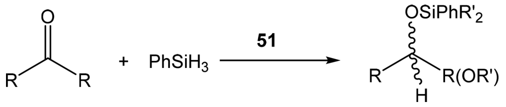
Furthermore, complex **51** was also investigated in the hydrosilylation of esters. The reaction proceeds under mild conditions with modest TOFs. In the case of ethyl acetate, PhSi(OEt)$_3$ and PhSiH(OEt)$_2$ were obtained in a 9:1 ratio after 5.5 h at room temperature using $PhSiH_3$. A much longer reaction time and/or heating to 80 °C were required for the hydrosilylation and ^{t}BuOAc.

10. HYDROBORATION REACTION

Catalytic hydroboration, the addition of B−H bonds across unsaturated bonds (C−C, C−N, and C−O), is a synthetically very useful reaction. The organoborane compounds formed can react with a variety of reagents to produce useful compounds, such as alcohols, amines, and alkyl halides. The most widely known reaction of the organoboranes is oxidation to produce alcohols, typically by hydrogen peroxide.

Chirik and co-workers[143] reported the catalytic hydroboration of substituted alkenes or alkynes with pinacolborane (HBPin) using cobalt methyl complexes (Scheme 45). The most active cobalt catalyst, **52**, was obtained by introducing a pyrrolidinyl substituent into the 4-position of the bis(imino)pyridine

Table 15. Selected Examples of Hydrosilylation of Ketones and Esters Catalyzed by Manganese Complex 51[a]



$PhSiH\{OCH(Me)(4\text{-}NMe_2\text{-}C_6H_4)\}_2$	$PhSi\{OCH(CF_3)(Ph)\}_3$	$PhSiH(OCy)_2$
>99	>99	>99
$PhSiH\{OCH(Me)(^nBu)\}_2$	$PhSiH\{OCH(Me)(2,4,6\text{-}Me\text{-}C_6H_2)\}_2$	$PhSi(OCy)_3$
>99	80	>99

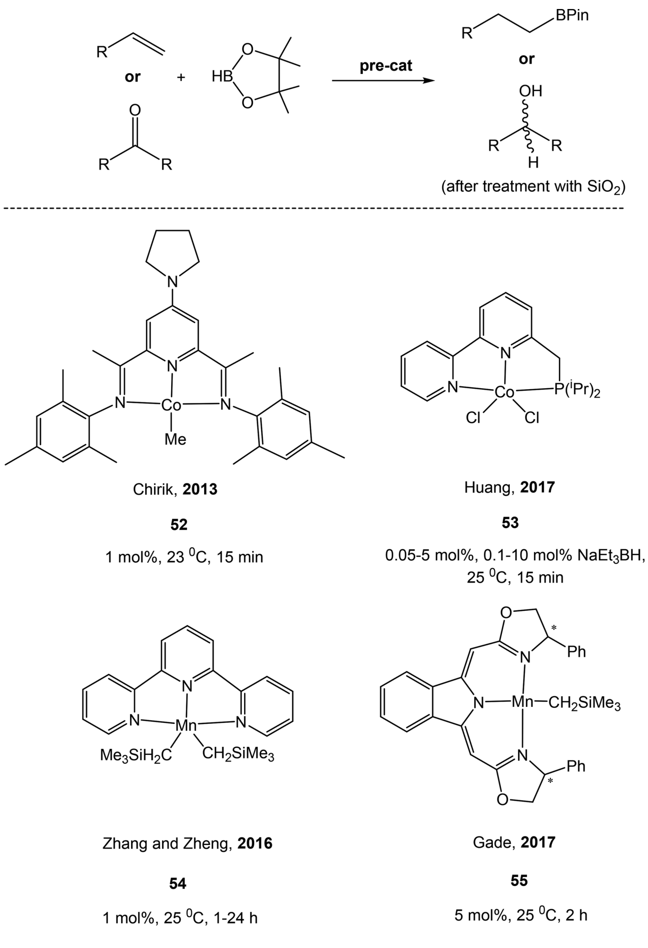
[a]Reaction conditions: substrate (0.33 mmol), $PhSiH_3$ (0.33 mmol), **51** (0.01−1 mol %), 25 °C.

ligand. Complex **52** exhibited the facile hydroboration of sterically hindered substrates such as 1-methylcyclohexene, α-pinene, and 2,3-dimethyl-2-butene. All of the catalytic hydroboration reactions proceed with high activity and anti-Markovnikov selectivity under ambient conditions (23 °C). Isomerization of internal olefins to the terminal position of the alkyl chain was observed under the catalytic conditions, providing a convenient method for the selective functionalization of the terminal position. Similarly, Huang and co-workers[144] showed that the cobalt complex **53** based on a PNN pincer ligand was a useful catalyst for the hydroboration reaction of alkenes with pinacolborane. Both aliphatic and aromatic alkenes undergo the hydroboration reaction to yield the corresponding products in excellent yield. Recently, Lu and co-workers reported the regioselctive hydroboration/cyclization of 1,6-enynes[145] and the asymmetric sequential hydroboration/hydrogenation of internal alkynes[146] catalyzed by cobalt pincer complexes.

Manganese-catalyzed hydroboration of alkenes, ketones. and aldehydes was reported by the groups of Zhang and Zheng (Scheme 45).[147] The Mn(II) complex **54**, based on the terpyridine ligand, is a precatalyst for the hydroboration of styrenes, exhibiting high Markovnikov regioselectivity. Excellent chemoselective hydroboration of ketones over alkenes was achieved in this case. Various functional groups were tolerated, and good catalytic activity for both alkenes (up to 93%) and ketones (up to 99%) was obtained with 1 mol % catalyst loading.

Very recently, Gade and co-workers[148] reported the chiral manganese alkyl complex **55** as a precatalyst for the enantioselective hydroboration of ketones (Scheme 45). Useful chiral alcohols were obtained in excellent yields and high enantiomeric excess (up to >99% ee). The hydroboration reaction works with both aryl alkyl and dialkyl ketone reduction under mild conditions (TOF > 450 h^{-1} at −40 °C), with low catalyst loadings (as low as 0.1 mol %).

Scheme 45. Hydroboration Reaction Catalyzed by Cobalt and Manganese Complexes



Chirik, **2013**

52

1 mol%, 23 °C, 15 min

Huang, **2017**

53

0.05-5 mol%, 0.1-10 mol% $NaEt_3BH$, 25 °C, 15 min

Zhang and Zheng, **2016**

54

1 mol%, 25 °C, 1-24 h

Gade, **2017**

55

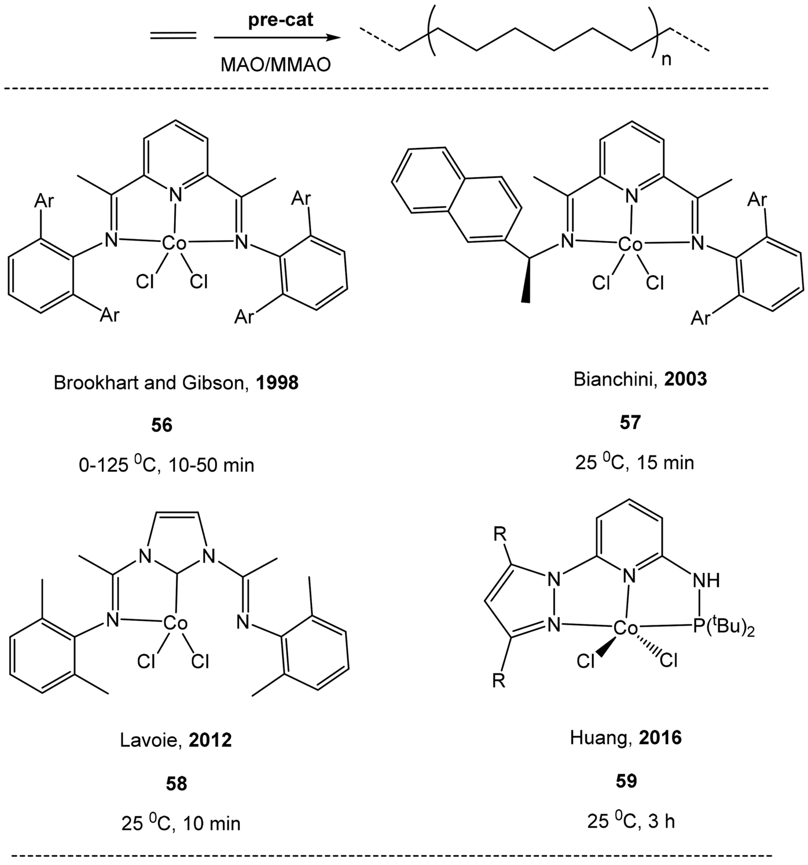
5 mol%, 25 °C, 2 h

11. OLEFIN OLIGO-/POLYMERIZATION

In 1998, Brookhart and co-workers[149] and Gibson and co-workers[150] independently reported bis(arylimino)pyridine iron and cobalt pincer complexes as catalysts for ethylene oligo-/polymerization (Scheme 46). The ethylene polymerization using **56** proceeds in the presence of methylalumoxane (MAO) or modified methylaluminoxane (MMAO) as an activator. High activity of the ethylene polymerization reaction (up to 17.0 × 10^6 g of PE mol^{-1} h^{-1}) was obtained using cobalt complexes.

Moreover, in 2003 Bianchini and co-workers[151] reported the NNN pincer Co(II) dichloro complex **57** for the oligomerization reaction of ethylene (Scheme 46). In the presence of methylaluminoxane (MAO), the catalytic reaction proceeds with complete selectivity to linear α-olefins. Furthermore, Lavoie and co-workers[152] reported a bis(imino)pyrimidin-2-ylidene-based cobalt(II) chroride complex (**58**) for ethylene polymerization reaction in the presence of MAO cocatalyst (Scheme 46). Recently, Huang and co-workers[153] reported the PNN pincer ligand based cobalt complex **59** for regio- and

Scheme 46. Oligo-/Polymerization of Ethylene Catalyzed by Cobalt Complexes



stereoselective polymerization of 1,3-butadiene in the presence of the activator.

12. CONCLUSIONS AND FUTURE PERSPECTIVE

As described, significant achievements have been made in homogeneous catalysis by cobalt and manganese pincer complexes in the past few years. Particularly remarkable is the surge in catalytic systems using manganese pincer complexes that were disclosed within the last couple of years, in comparison to the case for iron and cobalt pincer catalysts. Pincer complexes derived from the abundant and less toxic cobalt and manganese proved to be effective catalysts for hydrogenation, dehydrogenation, C−C bond formation, hydrosilylation, hydroboration, cycloaddition, and other related reactions. Several of the reported catalytic applications are environmentally benign and atom efficient and could potentially be industrially useful. These catalysts can exhibit high catalytic activities and high turnover numbers, in some cases comparable with those of noble-metal congeners. Moreover, in a few cases they can be effective in reactions not reported for noble metals. It is worth noting that mechanistic investigations of cobalt and manganese metal catalyzed reactions have played a significant role in establishing the field at the current level. For further progress in this field, a detailed understanding of the origins of the reactivity and unusual selectivity patterns that distinguish base-metal catalysts from their noble-metal counterparts can play a pivotal role.

Although significant progress has been made with cobalt and manganese pincer catalysis, the potential of these complexes has yet to be explored. In terms of further development, milder reaction conditions, greater functional group tolerance, and higher TONs and TOFs need to be targeted. Moreover, chiral cobalt and manganese pincer complexes for enantioselective catalysis are still in their infancy and further studies are envisioned.

We hope that this review will foster more research in this exciting field of chemistry and will lead to new and interesting discoveries.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) *Ligand Design in Metal Chemistry: Reactivity and Catalysis*; Stradiotto, M.; Lundgren, R. J., Eds.; Wiley-VCH: Weinheim, Germany, 2016.

(2) (a) *Organometallic Pincer Chemistry*; Van Koten, G.; Milstein, D., Eds.; Springer, 2012. (b) Morales-Morales, D. *Pincer Compounds: Chemistry and Applications*; Elsevier: Amsterdam, 2018. (c) Peris, E.;

Crabtree, R. H. Key factors in pincer ligand design. *Chem. Soc. Rev.* **2018**, *47*, 1959−1968 and references therein. .

(3) (a) Khusnutdinova, J. R.; Milstein, D. Metal−Ligand Cooperation. *Angew. Chem., Int. Ed.* **2015**, *54*, 12236−12273. (b) Milstein, D. Metal-Ligand Cooperation by Aromatization-Dearomatization as a Tool in Single Bond Activation. *Philos. Trans. R. Soc., A* **2015**, *373*, 20140189. (c) Gunanathan, C.; Milstein, D. *Bifunctional Molecular Catalysis*; Springer: Berlin, Heidelberg, 2011; pp 55.

(4) (a) Xiao-Feng, W. *Transition Metal-Catalyzed Heterocycle Synthesis via C-H Activation*; Wiley-VCH: Weinheim, Germany, 2015. (b) Díez-González, S.; Marion, N.; Nolan, S. P. N-Heterocyclic Carbenes in Late Transition Metal Catalysis. *Chem. Rev.* **2009**, *109*, 3612−3676. (c) Weissermel, K.; Arpe, H. J. *Industrial Organic Chemistry*, 4th ed.; Wiley-VCH: Weinheim, Germany, 2003. (d) Naota, T.; Takaya, H.; Murahashi, S.-I. Ruthenium-Catalyzed Reactions for Organic Synthesis. *Chem. Rev.* **1998**, *98*, 2599−2660.

(5) (a) Kumar, A.; Bhatti, T. M.; Goldman, A. S. Dehydrogenation of Alkanes and Aliphatic Groups by Pincer-Ligated Metal Complexes. *Chem. Rev.* **2017**, *117*, 12357−12384. (b) Valdés, H.; García-Eleno, M. A.; Canseco-Gonzalez, D.; Morales-Morales, D. Recent Advances in Catalysis with Transition-Metal Pincer Compounds. *ChemCatChem* **2018**, *10*, 3136. (c) Gunanathan, C.; Milstein, D. Applications of Acceptorless Dehydrogenation and Related Transformations in Chemical Synthesis. *Science* **2013**, *341*, 1229712. (d) Gunanathan, C.; Milstein, D. Bond Activation and Catalysis by Ruthenium Pincer Complexes. *Chem. Rev.* **2014**, *114*, 12024−12087.

(6) (a) Obligacion, J. V.; Chirik, P. J. Earth-abundant Transition Metal Catalysts for Alkene Hydrosilylation and Hydroboration. *Nature Rev. Chem.* **2018**, *2*, 15−34. (b) Obligacion, J. V.; Zhong, H.; Chirik, P. J. Insights into Activation of Cobalt Pre-Catalysts for C(*sp*2)−H Functionalization. *Isr. J. Chem.* **2017**, *57*, 1032−1036.

(7) Powers, I. G.; Uyeda, C. Metal−Metal Bonds in Catalysis. *ACS Catal.* **2017**, *7*, 936−958.

(8) Sun, J.; Deng, L. Cobalt Complex-Catalyzed Hydrosilylation of Alkenes and Alkynes. *ACS Catal.* **2016**, *6*, 290−300.

(9) (a) Zell, T.; Milstein, D. Hydrogenation and Dehydrogenation Iron Pincer Catalysts Capable of Metal−Ligand Cooperation by Aromatization/Dearomatization. *Acc. Chem. Res.* **2015**, *48*, 1979−1994. (b) Bauer, I.; Knolker, H.-J. Iron Catalysis in Organic Synthesis. *Chem. Rev.* **2015**, *115*, 3170−3387. (c) Morris, R. H. Exploiting Metal−Ligand Bifunctional Reactions in the Design of Iron Asymmetric Hydrogenation Catalysts. *Acc. Chem. Res.* **2015**, *48*, 1494−1502. (d) Chirik, P. J. Iron- and Cobalt-Catalyzed Alkene Hydrogenation: Catalysis with Both Redox-Active and Strong Field Ligands. *Acc. Chem. Res.* **2015**, *48*, 1687−1695. (e) Junge, K.; Schröder, K.; Beller, M. Homogeneous Catalysis Using Iron Complexes: Recent Developments in Selective Reductions. *Chem. Commun.* **2011**, *47*, 4849−4859. (f) Zell, T.; Langer, R. From Ruthenium to Iron and Manganese-A Mechanistic View on Challenges and Design Principles of Base-Metal Hydrogenation Catalysts. *ChemCatChem* **2018**, *10*, 1930−1940. (g) Gorgas, N.; Kirchner, K. Isoelectronic Manganese and Iron Hydrogenation/Dehydrogenation Catalysts: Similarities and Divergences. *Acc. Chem. Res.* **2018**, *51*, 1558−1569.

(10) (a) Murugesan, S.; Kirchner, K. Non-precious Metal Complexes with an Anionic PCP Pincer Architecture. *Dalton Trans.* **2016**, *45*, 416−439. (b) Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A. Catalytic (de)Hydrogenation Promoted by Non-precious metals − Co, Fe and Mn: Recent Advances in an Emerging Field. *Chem. Soc. Rev.* **2018**, *47*, 1459−1483.

(11) (a) Garbe, M.; Junge, K.; Beller, M. Homogeneous Catalysis by Manganese-Based Pincer Complexes. *Eur. J. Org. Chem.* **2017**, *2017*, 4344−4362. (b) Kallmeier, F.; Kempe, R. Manganese Complexes for (De)Hydrogenation Catalysis: A Comparison to Cobalt and Iron Catalysts. *Angew. Chem., Int. Ed.* **2018**, *57*, 46−60. (c) Maji, B.; Barman, M. K. Recent Developments of Manganese Complexes for Catalytic Hydrogenation and Dehydrogenation Reactions. *Synthesis* **2017**, *49*, 3377−3393.

(12) Vispute, T. P.; Zhang, H.; Sanna, A.; Xiao, R.; Huber, G. W. Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils. *Science* **2010**, *330*, 1222−1227.

(13) Tuck, C. O.; Perez, E.; Horvath, I. T.; Sheldon, R. A.; Poliakoff, M. Valorization of Biomass: Deriving More Value from Waste. *Science* **2012**, *337*, 695−699.

(14) Gnanaprakasam, B.; Zhang, J.; Milstein, D. Direct Synthesis of Imines from Alcohols and Amines with Liberation of H_2. *Angew. Chem., Int. Ed.* **2010**, *49*, 1468−1471.

(15) (a) Nakajima, Y.; Okamoto, Y.; Chang, Y.-H.; Ozawa, F. Synthesis, Structures, and Reactivity of Ruthenium Complexes with PNP-pincer Type Phosphaalkene Ligands. *Organometallics* **2013**, *32*, 2918−2925. (b) Musa, S.; Fronton, S.; Vaccaro, L.; Gelman, D. Bifunctional Ruthenium(II) PCP Pincer Complexes and Their Catalytic Activity in Acceptorless Dehydrogenative Reactions. *Organometallics* **2013**, *32*, 3069−3073. (c) Xu, C.; Goh, L. Y.; Pullarkat, S. A. Efficient Iridium-Thioether-Dithiolate Catalyst for β-Alkylation of Alcohols and Selective Imine Formation via N-Alkylation Reactions. *Organometallics* **2011**, *30*, 6499−6502. (d) Esteruelas, M. A.; Lezáun, V.; Martínez, A.; Oliván, M.; Oñate, E. Osmium Hydride Acetylacetonate Complexes and Their Application in Acceptorless Dehydrogenative Coupling of Alcohols and Amines and for the Dehydrogenation of Cyclic Amines. *Organometallics* **2017**, *36*, 2996−3004. (e) Esteruelas, M. A.; Honczek, N.; Oliván, M.; Oñate, E.; Valencia, M. Direct Access to POP-Type Osmium(II) and Osmium(IV) Complexes: Osmium a Promising Alternative to Ruthenium for the Synthesis of Imines from Alcohols and Amines. *Organometallics* **2011**, *30*, 2468−2471.

(16) Zhang, G.; Hanson, S. K. Cobalt-Catalyzed Acceptorless Alcohol Dehydrogenation: Synthesis of Imines from Alcohols and Amines. *Org. Lett.* **2013**, *15*, 650−653.

(17) Mukherjee, A.; Nerush, A.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Espinosa Jalapa, N. A.; Milstein, D. Manganese-Catalyzed Environmentally Benign Dehydrogenative Coupling of Alcohols and Amines to Form Aldimines and H_2: A Catalytic and Mechanistic Study. *J. Am. Chem. Soc.* **2016**, *138*, 4298−4301.

(18) Mastalir, M.; Glatz, M.; Gorgas, N.; Stöger, B.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Kirchner, K. Divergent Coupling of Alcohols and Amines Catalyzed by Isoelectronic Hydride Mn^I and Fe^{II} PNP Pincer Complexes. *Chem. - Eur. J.* **2016**, *22*, 12316−12320.

(19) Bauer, J. O.; Chakraborty, S.; Milstein, D. Manganese-Catalyzed Direct Deoxygenation of Primary Alcohols. *ACS Catal.* **2017**, *7*, 4462−4466.

(20) Das, U. K.; Ben-David, Y.; Diskin-Posner, Y.; Milstein, D. N-Substituted Hydrazones by Manganese-Catalyzed Coupling of Alcohols with Hydrazine: Borrowing Hydrogen and Acceptorless Dehydrogenation in One System. *Angew. Chem., Int. Ed.* **2018**, *57*, 2179−2182.

(21) Chakraborty, S.; Das, U. K.; Ben-David, Y.; Milstein, D. Manganese Catalyzed α-Olefination of Nitriles by Primary Alcohols. *J. Am. Chem. Soc.* **2017**, *139*, 11710−11713.

(22) (a) Michlik, S.; Kempe, R. A Sustainable Catalytic Pyrrole Synthesis. *Nat. Chem.* **2013**, *5*, 140−144. (b) Srimani, D.; Ben-David, Y.; Milstein, D. Direct Synthesis of Pyrroles by Dehydrogenative Coupling of β-Aminoalcohols with Secondary Alcohols Catalyzed by Ruthenium Pincer Complexes. *Angew. Chem., Int. Ed.* **2013**, *52*, 4012−4015. (c) Zhang, M.; Neumann, H.; Beller, M. Selective Ruthenium-Catalyzed Three-Component Synthesis of Pyrroles. *Angew. Chem., Int. Ed.* **2013**, *52*, 597−601. (d) Michlik, S.; Kempe, R. Regioselectively Functionalized Pyridines from Sustainable Resources. *Angew. Chem., Int. Ed.* **2013**, *52*, 6326−6329. (e) Srimani, D.; Ben-David, Y.; Milstein, D. Direct Synthesis of Pyridines and Quinolines by Coupling of γ-Amino-alcohols with Secondary Alcohols Liberating H_2 Catalyzed by Ruthenium Pincer Complexes. *Chem. Commun.* **2013**, *49*, 6632−6634.

(23) Daw, P.; Chakraborty, S.; Garg, J. A.; Ben-David, Y.; Milstein, D. Direct Synthesis of Pyrroles by Dehydrogenative Coupling of Diols and Amines Catalyzed by Cobalt Pincer Complexes. *Angew. Chem., Int. Ed.* **2016**, *55*, 14373−14377.

(24) Daw, P.; Ben-David, Y.; Milstein, D. Direct Synthesis of Pyrroles by Dehydrogenative Coupling of Diols and Amines Catalyzed by Cobalt Pincer Complexes. *ACS Catal.* **2017**, *7*, 7456−7460.

(25) Midya, S. P.; Landge, V. G.; Sahoo, M. K.; Rana, J.; Balaraman, E. Cobalt-catalyzed Acceptorless Dehydrogenative Coupling of Aminoalcohols with Alcohols: Direct Access to Pyrrole, Pyridine and Pyrazine Derivatives. *Chem. Commun.* **2018**, *54*, 90−93.

(26) Kallmeier, F.; Dudziec, B.; Irrgang, T.; Kempe, R. Manganese-Catalyzed Sustainable Synthesis of Pyrroles from Alcohols and Amino Alcohols. *Angew. Chem., Int. Ed.* **2017**, *56*, 7261−7265.

(27) Zhang, G.; Wu, J.; Zeng, H.; Zhang, S.; Yin, Z.; Zheng, S. Cobalt-Catalyzed α-Alkylation of Ketones with Primary Alcohols. *Org. Lett.* **2017**, *19*, 1080−1083.

(28) Mastalir, M.; Glatz, M.; Pittenauer, E.; Allmaier, G.; Kirchner, K. Sustainable Synthesis of Quinolines and Pyrimidines Catalyzed by Manganese PNP Pincer Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 15543−15546.

(29) Deibl, N.; Kempe, R. Manganese-Catalyzed Multicomponent Synthesis of Pyrimidines from Alcohols and Amidines. *Angew. Chem., Int. Ed.* **2017**, *56*, 1663−1666.

(30) Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic Chemistry*; Oxford University Press, 2000.

(31) Magano, J.; Dunetz, J. R. Large-Scale Applications of Transition Metal-Catalyzed Couplings for the Synthesis of Pharmaceuticals. *Chem. Rev.* **2011**, *111*, 2177−2250.

(32) Sperotto, E.; van Klink, G. P. M.; van Koten, G.; de Vries, J. G. The Mechanism of the Modified Ullmann Reaction. *Dalton Trans.* **2010**, *39*, 10338−10351.

(33) Huang, L.; Arndt, M.; Gooßen, K.; Heydt, H.; Gooßen, L. J. Late Transition Metal-Catalyzed Hydroamination and Hydroamidation. *Chem. Rev.* **2015**, *115*, 2596−2697.

(34) Rösler, S.; Ertl, M.; Irrgang, T.; Kempe, R. Cobalt-Catalyzed Alkylation of Aromatic Amines by Alcohols. *Angew. Chem., Int. Ed.* **2015**, *54*, 15046−15050.

(35) Zhang, G.; Yin, Z.; Zheng, S. Cobalt-Catalyzed N-Alkylation of Amines with Alcohols. *Org. Lett.* **2016**, *18*, 300−303.

(36) Mastalir, M.; Tomsu, G.; Pittenauer, E.; Allmaier, G.; Kirchner, K. Co(II) PCP Pincer Complexes as Catalysts for the Alkylation of Aromatic Amines with Primary Alcohols. *Org. Lett.* **2016**, *18*, 3462−3465.

(37) Yin, Z.; Zeng, H.; Wu, J.; Zheng, S.; Zhang, G. Cobalt-Catalyzed Synthesis of Aromatic, Aliphatic, and Cyclic Secondary Amines via a "Hydrogen-Borrowing" Strategy. *ACS Catal.* **2016**, *6*, 6546−6550.

(38) Midya, S. P.; Pitchaimani, J.; Landge, V. G.; Madhu, V.; Balaraman, E. Direct Access to N-Alkylated Amines and Imines via Acceptorless Dehydrogenative Coupling Catalyzed by a Cobalt(II)-NNN Pincer Complex. *Catal. Sci. Technol.* **2018**, *8*, 3469−3473.

(39) Elangovan, S.; Neumann, J.; Sortais, J. B.; Junge, K.; Darcel, C.; Beller, M. Efficient and selective *N*-alkylation of Amines with Alcohols Catalysed by Manganese Pincer Complexes. *Nat. Commun.* **2016**, *7*, 12641.

(40) Neumann, J.; Elangovan, S.; Spannenberg, A.; Junge, K.; Beller, M. Improved and General Manganese-Catalyzed N-Methylation of Aromatic Amines Using Methanol. *Chem. - Eur. J.* **2017**, *23*, 5410−5413.

(41) Bruneau-Voisine, A.; Wang, D.; Dorcet, V.; Roisnel, T.; Darcel, C.; Sortais, J.-B. Mono-*N*-methylation of Anilines with Methanol Catalyzed by a Manganese Pincer-complex. *J. Catal.* **2017**, *347*, 57−62.

(42) Mastalir, M.; Pittenauer, E.; Allmaier, G.; Kirchner, K. Manganese-Catalyzed Aminomethylation of Aromatic Compounds with Methanol as a Sustainable C1 Building Block. *J. Am. Chem. Soc.* **2017**, *139*, 8812−8815.

(43) Deibl, N.; Kempe, R. General and Mild Cobalt-Catalyzed C-Alkylation of Unactivated Amides and Esters with Alcohols. *J. Am. Chem. Soc.* **2016**, *138*, 10786−10789.

(44) Guo, L.; Liu, Y.; Yao, W.; Leng, X.; Huang, Z. Iridium-Catalyzed Selective α-Alkylation of Unactivated Amides with Primary Alcohols. *Org. Lett.* **2013**, *15*, 1144−1147.

(45) Freitag, F.; Irrgang, T.; Kempe, R. Cobalt-Catalyzed Alkylation of Secondary Alcohols with Primary Alcohols via Borrowing Hydrogen/Hydrogen Autotransfer. *Chem. - Eur. J.* **2017**, *23*, 12110−12113.

(46) Peña-López, M.; Piehl, P.; Elangovan, S.; Neumann, H.; Beller, M. Manganese-Catalyzed Hydrogen-Autotransfer C−C Bond Formation: α-Alkylation of Ketones with Primary Alcohols. *Angew. Chem., Int. Ed.* **2016**, *55*, 14967−14971.

(47) Boyle, G. *Renewable Energy: Power for a Sustainable Future*, 3rd Ed., Oxford University Press, 2012.

(48) *Biofuels, Alternative Feedstocks and Conversion Processes*, 1st ed.; Pandey, A., Larroche, C., Ricke, S., Dussap, C.-G., Gnansounou, E., Eds.; Academic Press, 2011.

(49) Harvey, B. G.; Meylemans, H. A. The role of Butanol in the Development of Sustainable Fuel Technologies. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 2−9.

(50) (a) Xie, Y.; Ben-David, Y.; Shimon, L. J. W.; Milstein, D. Highly Efficient Process for Production of Biofuel from Ethanol Catalyzed by Ruthenium Pincer Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 9077−9080. (b) Tseng, K. T.; Lin, S.; Kampf, J. W.; Szymczak, N. K. Upgrading Ethanol to 1-Butanol with a Homogeneous Air-stable Ruthenium Catalyst. *Chem. Commun.* **2016**, *52*, 2901−2904. (c) Dowson, G. R. M.; Haddow, M. F.; Lee, J.; Wingad, R. L.; Wass, D. F. Catalytic Conversion of Ethanol into an Advanced Biofuel: Unprecedented Selectivity for n-Butanol. *Angew. Chem., Int. Ed.* **2013**, *52*, 9005−9008. (d) Chakraborty, S.; Piszel, P. E.; Hayes, C. E.; Baker, R. T.; Jones, W. D. Highly Selective Formation of n-Butanol from Ethanol through the Guerbet Process: A Tandem Catalytic Approach. *J. Am. Chem. Soc.* **2015**, *137*, 14264−14267. (e) Wingad, R. L.; Gates, P. J.; Street, S. T. G.; Wass, D. F. Catalytic Conversion of Ethanol to n-Butanol Using Ruthenium P−N Ligand Complexes. *ACS Catal.* **2015**, *5*, 5822−5826 and references therein . (f) Koda, K.; Matsu-ura, T.; Obora, Y.; Ishii, Y. Guerbet Reaction of Ethanol to n-Butanol Catalyzed by Iridium Complexes. *Chem. Lett.* **2009**, *38*, 838−839.

(51) Fu, S.; Shao, Z.; Wang, Y.; Liu, Q. Manganese-Catalyzed Upgrading of Ethanol into 1-Butanol. *J. Am. Chem. Soc.* **2017**, *139*, 11941−11948.

(52) Kulkarni, N. V.; Brennessel, W. W.; Jones, W. D. Catalytic Upgrading of Ethanol to n-Butanol via Manganese-Mediated Guerbet Reaction. *ACS Catal.* **2018**, *8*, 997−1002.

(53) (a) Moran, J.; Preetz, A.; Mesch, R. A.; Krische, M. J. Iridium-catalysed Direct C−C Coupling of Methanol and Allenes. *Nat. Chem.* **2011**, *3*, 287−290. (b) Chan, L. K. M.; Poole, D. L.; Shen, D.; Healy, M. P.; Donohoe, T. J. Rhodium-catalyzed Ketone Methylation Using Methanol Under Mild Conditions: Formation of α-Branched Products. *Angew. Chem., Int. Ed.* **2014**, *53*, 761−765. (c) Alberico, E.; Nielsen, M. Towards a Methanol Economy Based on Homogeneous Catalysis: Methanol to H_2 and CO_2 to Methanol. *Chem. Commun.* **2015**, *51*, 6714−6725. (d) Sam, B.; Breit, B.; Krische, M. J. Paraformaldehyde and Methanol as C1 Feedstocks in Metal-Catalyzed C-C Couplings of π-Unsaturated Reactants: Beyond Hydroformylation. *Angew. Chem., Int. Ed.* **2015**, *54*, 3267−3274. (e) Shen, D.; Poole, D. L.; Shotton, C. C.; Kornahrens, A. F.; Healy, M. P.; Donohoe, T. J. Hydrogen-Borrowing and Interrupted-Hydrogen-Borrowing Reactions of Ketones and Methanol Catalyzed by Iridium. *Angew. Chem., Int. Ed.* **2015**, *54*, 1642−1645. (f) Heim, L. E.; Thiel, D.; Gedig, C.; Deska, J.; Prechtl, M. H. G. Bioinduced Room-Temperature Methanol Reforming. *Angew. Chem., Int. Ed.* **2015**, *54*, 10308−10312. (g) Nguyen, K. D.; Herkommer, D.; Krische, M. J. Enantioselective Formation of All-Carbon Quaternary Centers via C−H Functionalization of Methanol: Iridium-Catalyzed Diene Hydrohydroxymethylation. *J. Am. Chem. Soc.* **2016**, *138*, 14210−14213. (h) Filonenko, G. A.; Conley, M. P.; Coperet, C.; Lutz, M.; Hensen, E. J. M.; Pidko, E. A. The Impact of Metal−Ligand Cooperation in Hydrogenation of Carbon Dioxide Catalyzed by

Ruthenium PNP Pincer. *ACS Catal.* **2013**, *3*, 2522−2526. (i) Huff, C. A.; Sanford, M. S. Catalytic CO_2 Hydrogenation to Formate by a Ruthenium Pincer Complex. *ACS Catal.* **2013**, *3*, 2412−2416. (j) Muller, K.; Sun, Y.; Thiel, W. R. Ruthenium(II)-Phosphite Complexes as Catalysts for the Hydrogenation of Carbon Dioxide. *ChemCatChem* **2013**, *5*, 1340−1343.

(54) (a) Alberico, E.; Sponholz, P.; Cordes, C.; Nielsen, M.; Drexler, H.-J.; Baumann, W.; Junge, H.; Beller, M. Selective Hydrogen Production from Methanol with a Defined Iron Pincer Catalyst under Mild Conditions. *Angew. Chem., Int. Ed.* **2013**, *52*, 14162−14166. (b) Bielinski, E. A.; Förster, M.; Zhang, Y.; Bernskoetter, W. H.; Hazari, N.; Holthausen, M. C. Base-Free Methanol Dehydrogenation Using a Pincer-Supported Iron Compound and Lewis Acid Co-catalyst. *ACS Catal.* **2015**, *5*, 2404−2415. (c) Lane, E. M.; Hazari, N.; Bernskoetter, W. H. Iron-catalyzed urea synthesis: dehydrogenative coupling of methanol and amines. *Chem. Sci.* **2018**, *9*, 4003−4008.

(55) Andérez-Fernández, M.; Vogt, L. K.; Fischer, S.; Zhou, W.; Jiao, H.; Garbe, M.; Elangovan, S.; Junge, K.; Junge, H.; Ludwig, R.; Beller, M. A Stable Manganese Pincer Catalyst for the Selective Dehydrogenation of Methanol. *Angew. Chem., Int. Ed.* **2017**, *56*, 559−562.

(56) Tondreau, A. M.; Boncella, J. M. 1,2-Addition of Formic or Oxalic Acid to − $N\{CH_2CH_2(PiPr_2)\}_2$-Supported Mn(I) Dicarbonyl Complexes and the Manganese-Mediated Decomposition of Formic Acid. *Organometallics* **2016**, *35*, 2049−2052.

(57) Ji, M.; Dong, C.; Yang, X. Density Functional Theory Prediction of Cobalt Pincer Complexes for Catalytic Dehydrogenation of Ethanol. *J. Coord. Chem.* **2016**, *69*, 1380−1387.

(58) (a) Tlili, A.; Blondiaux, E.; Frogneux, X.; Cantat, T. Reductive Functionalization of CO2 with Amines: An Entry to Formamide, Formamidine and Methylamine Derivatives. *Green Chem.* **2015**, *17*, 157−168. (b) Hett, R.; Fang, Q. K.; Gao, Y.; Wald, S. A.; Senanayake, C. H. Large-Scale Synthesis of Enantio- and Diastereomerically Pure (*R*,*R*)-Formoterol. *Org. Process Res. Dev.* **1998**, *2*, 96−99.

(59) (a) Zhang, L.; Han, Z.; Zhao, X.; Wang, Z.; Ding, K. Highly Efficient Ruthenium-Catalyzed *N*-Formylation of Amines with H_2 and CO_2. *Angew. Chem., Int. Ed.* **2015**, *54*, 6186−6189. (b) Das Neves Gomes, C.; Jacquet, O.; Villiers, C.; Thuery, P.; Ephritikhine, M.; Cantat, T. A Diagonal Approach to Chemical Recycling of Carbon Dioxide: Organocatalytic Transformation for the Reductive Functionalization of CO_2. *Angew. Chem., Int. Ed.* **2012**, *51*, 187−190. (c) Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P. J.; Scopelliti, R.; Laurenczy, G.; Beller, M. A Well-Defined Iron Catalyst for the Reduction of Bicarbonates and Carbon Dioxide to Formates, Alkyl Formates, and Formamides. *Angew. Chem., Int. Ed.* **2010**, *49*, 9777−9780. (d) El Dine, T. M.; Evans, D.; Rouden, J.; Blanchet, J. Formamide Synthesis through Borinic Acid Catalysed Transamidation under Mild Conditions. *Chem. - Eur. J.* **2016**, *22*, 5894−5898.

(60) Chakraborty, S.; Gellrich, U.; Diskin-Posner, Y.; Leitus, G.; Avram, L.; Milstein, D. Manganese-Catalyzed N-Formylation of Amines by Methanol Liberating H2: A Catalytic and Mechanistic Study. *Angew. Chem., Int. Ed.* **2017**, *56*, 4229−4233.

(61) Espinosa-Jalapa, N. A.; Kumar, A.; Leitus, G.; Diskin-Posner, Y.; Milstein, D. Synthesis of Cyclic Imides by Acceptorless Dehydrogenative Coupling of Diols and Amines Catalyzed by a Manganese Pincer Complex. *J. Am. Chem. Soc.* **2017**, *139*, 11722−11725.

(62) Cupido, T.; Tulla-Puche, J.; Spengler, J.; Albericio, F. The synthesis of naturally occurring peptides and their analogs. *Curr. Opin. Drug Discovery Dev.* **2007**, *10*, 768−783.

(63) (a) Smith, M. B. *Compendium of Organic Synthetic Methods*; Wiley: New York, 2001; Vol. 9, p 100. (b) de Figueiredo, R. M.; Suppo, J.-S.; Campagne, J.-M. Nonclassical Routes for Amide Bond Formation. *Chem. Rev.* **2016**, *116*, 12029−12122.

(64) Gunanathan, C.; Ben-David, Y.; Milstein, D. Direct Synthesis of Amides From Alcohols and Amines with liberation of H_2. *Science* **2007**, *317*, 790−792.

(65) (a) Nordstrøm, L. U.; Vogt, H.; Madsen. Amide Synthesis from Alcohols and Amines by the Extrusion of Dihydrogen. R. *J. Am. Chem. Soc.* **2008**, *130*, 17672−17673. (b) Zweifel, T.; Naubron, J.-V.; Grützmacher, H. Catalyzed Dehydrogenative Coupling of Primary Alcohols with Water, Methanol, or Amines. *Angew. Chem., Int. Ed.* **2009**, *48*, 559−563. (c) Watson, A. J. A.; Maxwell, A. C.; Williams, J. M. J. Ruthenium-Catalyzed Oxidation of Alcohols into Amides. *Org. Lett.* **2009**, *11*, 2667−2670. (d) Chen, C.; Zhang, Y.; Hong, S. H. N-Heterocyclic Carbene Based Ruthenium-Catalyzed Direct Amide Synthesis from Alcohols and Secondary Amines: Involvement of Esters. *J. Org. Chem.* **2011**, *76*, 10005−10010. (e) Liu, X.; Jensen, K. F. Direct Oxidative Amidation of Aromatic Aldehydes Using Aqueous Hydrogen Peroxide in Continuous Flow Microreactor Systems. *Green Chem.* **2012**, *14*, 1471−1474. (f) Ortega, N.; Richter, C.; Glorius, F. N-Formylation of Amines by Methanol Activation. *Org. Lett.* **2013**, *15*, 1776−1779. (g) Kang, B.; Fu, Z.; Hong, S. H. Ruthenium-Catalyzed Redox-Neutral and Single-Step Amide Synthesis from Alcohol and Nitrile with Complete Atom Economy. *J. Am. Chem. Soc.* **2013**, *135*, 11704−11707. (h) Schleker, P. P. M.; Honeker, R.; Klankermayer, J.; Leitner, W. Catalytic Dehydrogenative Amide and Ester Formation with Rhenium−Triphos Complexes. *ChemCatChem* **2013**, *5*, 1762−1764. (i) Saha, B.; Sengupta, G.; Sarbajna, A.; Dutta, I.; Bera, J. K. Amide Synthesis From Alcohols and Amines catalyzed by a RuII−N-heterocyclic carbene (NHC)−carbonyl complex. *J. Organomet. Chem.* **2014**, *771*, 124−130. (j) Spasyuk, D.; Vicent, C.; Gusev, D. G. Chemoselective Hydrogenation of Carbonyl Compounds and Acceptorless Dehydrogenative Coupling of Alcohols. *J. Am. Chem. Soc.* **2015**, *137*, 3743−3746 and references therein .

(66) Kumar, A.; Espinosa-Jalapa, N. A.; Leitus, G.; Diskin-Posner, Y.; Avram, L.; Milstein, D. Direct Synthesis of Amides by Dehydrogenative Coupling of Amines with either Alcohols or Esters: Manganese Pincer Complex as Catalyst. *Angew. Chem., Int. Ed.* **2017**, *56*, 14992−14996.

(67) Nguyen, D. H.; Trivelli, X.; Capet, F.; Paul, J.- F.; Dumeignil, F.; Gauvin, R. M. Manganese Pincer Complexes for the Base-Free, Acceptorless Dehydrogenative Coupling of Alcohols to Esters: Development, Scope, and Understanding. *ACS Catal.* **2017**, *7*, 2022−2032.

(68) Xu, R.; Chakraborty, S.; Yuan, H.; Jones, W. D. Acceptorless, Reversible Dehydrogenation and Hydrogenation of N-Heterocycles with a Cobalt Pincer Catalyst. *ACS Catal.* **2015**, *5*, 6350−6354.

(69) Noyori, R. Asymmetric Catalysis: Science and Opportunities. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008−2022.

(70) (a) Blaser, H.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. Selective Hydrogenation for Fine Chemicals: Recent Trends and New Developments. *Adv. Synth. Catal.* **2003**, *345*, 103−151. (b) Lennon, I. C.; Casy, G.; Johnson, N. B. Effective Commercialisation of Asymmetric Hydrogenation Technology. *Chem. Today* **2003**, *21*, 63−67. (c) Lennon, I. C.; Moran, P. H. Asymmetric Hydrogenation of Pharmaceutically Interesting Substrates. *Curr. Opin. Drug Discovery Dev.* **2003**, *6*, 855−875.

(71) Zhang, G.; Scott, B. L.; Hanson, S. K. Mild and Homogeneous Cobalt-catalyzed Hydrogenation of C═C, C═O, and C═N bonds. *Angew. Chem., Int. Ed.* **2012**, *51*, 12102−12106.

(72) Gärtner, D.; Welther, A.; Rad, B. R.; Wolf, R.; von Wangelin, A. J. Heteroatom-free arene-cobalt and arene-iron catalysts for hydrogenations. *Angew. Chem., Int. Ed.* **2014**, *53*, 3722−3726.

(73) Roesler, S.; Obenauf, J.; Kempe, R. A Highly Active and Easily Accessible Cobalt Catalyst for Selective Hydrogenation of C═O Bonds. *J. Am. Chem. Soc.* **2015**, *137*, 7998−8001.

(74) Elangovan, S.; Topf, C.; Fischer, S.; Jiao, H.; Spannenberg, A.; Baumann, W.; Ludwig, R.; Junge, K.; Beller, M. Selective Catalytic Hydrogenations of Nitriles, Ketones, and Aldehydes by Well-Defined Manganese Pincer Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 8809−8814.

(75) Kallmeier, F.; Irrgang, T.; Dietel, T.; Kempe, R. Highly Active and Selective Manganese C═O Bond Hydrogenation Catalysts: The Importance of the Multidentate Ligand, the Ancillary Ligands, and the Oxidation State. *Angew. Chem., Int. Ed.* **2016**, *55*, 11806−11809.

(76) Glatz, M.; Stöger, B.; Himmelbauer, D.; Veiros, L. F.; Kirchner, K. Chemoselective Hydrogenation of Aldehydes under Mild, Base-

Free Conditions: Manganese Outperforms Rhenium. *ACS Catal.* **2018**, *8*, 4009−4016.

(77) Zhang, D.; Zhu, E.; Lin, Z.; Wei, Z.-B.; Li, Y.; Gao, J. Enantioselective Hydrogenation of Ketones Catalyzed by Chiral Cobalt Complexes Containing PNNP Ligand. *Asian J. Org. Chem.* **2016**, *5*, 1323−1326.

(78) Widegren, M. B.; Harkness, G. J.; Slawin, A. M. Z.; Cordes, D. B.; Clarke, M. L. A Highly Active Manganese Catalyst for Enantioselective Ketone and Ester Hydrogenation. *Angew. Chem., Int. Ed.* **2017**, *56*, 5825−5828.

(79) Garbe, M.; Junge, K.; Walker, S.; Wei, Z.; Jiao, H.; Spannenberg, A.; Bachmann, S.; Scalone, M.; Beller, M. Manganese-(I)-Catalyzed Enantioselective Hydrogenation of Ketones Using a Defined Chiral PNP Pincer Ligand. *Angew. Chem., Int. Ed.* **2017**, *56*, 11237−11241.

(80) Eisenstein, O.; Crabtree, R. H. Outer Sphere Hydrogenation Catalysis. *New J. Chem.* **2013**, *37*, 21−27.

(81) Zhang, G.; Hanson, S. K. Cobalt-catalyzed Transfer Hydrogenation of C═O and C═N bonds. *Chem. Commun.* **2013**, *49*, 10151−10153.

(82) ter Halle, R.; Bréhéret, A.; Schulz, E. C.; Pinel; Lemaire, M. Chiral Nitrogen-metal Complexes for the Asymmetric Reduction of Ketones. *Tetrahedron: Asymmetry* **1997**, *8*, 2101−2108.

(83) Perez, M.; Elangovan, S.; Spannenberg, A.; Junge, K.; Beller, M. Molecularly Defined Manganese Pincer Complexes for Selective Transfer Hydrogenation of Ketones. *ChemSusChem* **2017**, *10*, 83−86.

(84) Zirakzadeh, A.; de Aguiar, S. R. M. M.; Stöger, B.; Widhalm, M.; Kirchner, K. Enantioselective Transfer Hydrogenation of Ketones Catalyzed by a Manganese Complex Containing an Unsymmetrical Chiral PNP′ Tridentate Ligand. *ChemCatChem* **2017**, *9*, 1744−1748.

(85) Pouilloux, Y.; Autin, F.; Barrault, J. Selective Hydrogenation of Methyl Oleate into Unsaturated Alcohols: Relationships Between Catalytic Properties and Composition of Cobalt−tin Catalysts. *Catal. Today* **2000**, *63*, 87−100 and references therein .

(86) Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. Efficient Homogeneous Catalytic Hydrogenation of Esters to Alcohols. *Angew. Chem., Int. Ed.* **2006**, *45*, 1113−1115.

(87) Werkmeister, S.; Junge, K.; Wendt, B.; Alberico, E.; Jiao, H.; Baumann, W.; Junge, H.; Gallou, F.; Beller, M. Hydrogenation of Esters to Alcohols with a Well-Defined Iron Complex. *Angew. Chem., Int. Ed.* **2014**, *53*, 8722−8726.

(88) Srimani, D.; Mukherjee, A.; Goldberg, A. F.; Leitus, G.; Diskin Posner, Y.; Shimon, L. J.; Ben-David, Y.; Milstein, D. Cobalt-Catalyzed Hydrogenation of Esters to Alcohols: Unexpected Reactivity Trend Indicates Ester Enolate Intermediacy. *Angew. Chem., Int. Ed.* **2015**, *54*, 12357−12360.

(89) Yuwen, J.; Chakraborty, S.; Brennessel, W. W.; Jones, W. D. Additive-Free Cobalt-Catalyzed Hydrogenation of Esters to Alcohols. *ACS Catal.* **2017**, *7*, 3735−3740.

(90) Junge, K.; Wendt, B.; Cingolani, A.; Spannenberg, A.; Wei, Z.; Jiao, H.; Beller, M. Cobalt Pincer Complexes for Catalytic Reduction of Carboxylic Acid Esters. *Chem. - Eur. J.* **2018**, *24*, 1046−1052.

(91) Korstanje, T. J.; Ivar van der Vlugt, J.; Elsevier, C. J.; de Bruin, B. Hydrogenation of Carboxylic Acids with a Homogeneous Cobalt Catalyst. *Science* **2015**, *350*, 298−302.

(92) Elangovan, S.; Garbe, M.; Jiao, H.; Spannenberg, A.; Junge, K.; Beller, M. Hydrogenation of Esters to Alcohols Catalyzed by Defined Manganese Pincer Complexes. *Angew. Chem., Int. Ed.* **2016**, *55*, 15364−15368.

(93) Espinosa-Jalapa, N. A.; Nerush, A.; Shimon, L. J. W.; Leitus, G.; Avram, L.; Ben-David, Y.; Milstein, D. Manganese-Catalyzed Hydrogenation of Esters to Alcohols. *Chem. - Eur. J.* **2017**, *23*, 5934−5938.

(94) van Putten, R.; Uslamin, E. A.; Garbe, M.; Liu, C.; Gonzalez-de-Castro, A.; Lutz, M.; Junge, K.; Hensen, E. J. M.; Beller, M.; Lefort, L.; Pidko, E. A. Non-Pincer-Type Manganese Complexes as Efficient Catalysts for the Hydrogenation of Esters. *Angew. Chem., Int. Ed.* **2017**, *56*, 7531−7534.

(95) (a) Gomez, S.; Peters, J. A.; Maschmeyer, T. The Reductive Amination of Aldehydes and Ketones and the Hydrogenation of Nitriles: Mechanistic Aspects and Selectivity Control. *Adv. Synth. Catal.* **2002**, *344*, 1037−1057. (b) Srimani, D.; Feller, M.; Ben-David, Y.; Milstein, D. Catalytic Coupling of Nitriles with Amines to Selectively Form Imines Under Mild Hydrogen Pressure. *Chem. Commun.* **2012**, *48*, 11853−11855.

(96) Mukherjee, A.; Srimani, D.; Chakraborty, S.; Ben-David, Y.; Milstein, D. Selective Hydrogenation of Nitriles to Primary Amines Catalyzed by a Cobalt Pincer Complex. *J. Am. Chem. Soc.* **2015**, *137*, 8888−8891.

(97) Shao, Z.; Fu, S.; Wei, M.; Zhou, S.; Liu, Q. Mild and Selective Cobalt-Catalyzed Chemodivergent Transfer Hydrogenation of Nitriles. *Angew. Chem., Int. Ed.* **2016**, *55*, 14653−14657.

(98) Elangovan, S.; Topf, C.; Fischer, S.; Jiao, H.; Spannenberg, A.; Baumann, W.; Ludwig, R.; Junge, K.; Beller, M. Selective Catalytic Hydrogenations of Nitriles, Ketones, and Aldehydes by Well-Defined Manganese Pincer Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 8809−8814.

(99) Papa, V.; Cabrero-Antonino, J. R.; Alberico, E.; Spanneberg, A.; Junge, K.; Junge, H.; Beller, M. Efficient and Selective Hydrogenation of Amides to Alcohols and Amines using a well-defined Manganese−PNN Pincer Complex. *Chem. Sci.* **2017**, *8*, 3576−3585.

(100) Kar, S.; Goeppert, A.; Kothandaraman, J.; Prakash, G. K. S. Manganese-Catalyzed Sequential Hydrogenation of CO2 to Methanol via Formamide. *ACS Catal.* **2017**, *7*, 6347−6351.

(101) Knijnenburg, Q.; Horton, A. D.; van der Heijden, H.; Kooistra, T. M.; Hetterscheid, D. G. H.; Smits, J. M. M.; de Bruin, B.; Budzelaar, P. H. M.; Gal, A. W. Olefin Hydrogenation Using Diimine Pyridine Complexes of Co and Rh. *J. Mol. Catal. A: Chem.* **2005**, *232*, 151−159.

(102) Zhang, G.; Vasudevan, K. V.; Scott, B. L.; Hanson, S. K. Understanding the Mechanisms of Cobalt-Catalyzed Hydrogenation and Dehydrogenation Reactions. *J. Am. Chem. Soc.* **2013**, *135*, 8668−8681.

(103) Tokmic, K.; Markus, C. R.; Zhu, L.; Fout, A. R. Well-Defined Cobalt(I) Dihydrogen Catalyst: Experimental Evidence for a Co(I)/Co(III) Redox Process in Olefin Hydrogenation. *J. Am. Chem. Soc.* **2016**, *138*, 11907−11913.

(104) Monfette, S.; Turner, Z. R.; Semproni, S. P.; Chirik, P. J. Enantiopure C1-Symmetric Bis(imino)pyridine Cobalt Complexes for Asymmetric Alkene Hydrogenation. *J. Am. Chem. Soc.* **2012**, *134*, 4561−4564.

(105) Friedfeld, M. R.; Shevlin, M.; Margulieux, G. W.; Campeau, L.-C.; Chirik, P. J. Cobalt-Catalyzed Enantioselective Hydrogenation of Minimally Functionalized Alkenes: Isotopic Labeling Provides Insight into the Origin of Stereoselectivity and Alkene Insertion Preferences. *J. Am. Chem. Soc.* **2016**, *138*, 3314−3324.

(106) Friedfeld, M. R.; Shevlin, M.; Hoyt, J. M.; Krska, S. W.; Tudge, M. T.; Chirik, P. J. Cobalt Precursors for High-Throughput Discovery of Base Metal Asymmetric Alkene Hydrogenation Catalysts. *Science* **2013**, *342*, 1076−1080.

(107) Zhang, G.; Yin, Z.; Tan, J. Cobalt(II)-catalysed Transfer Hydrogenation of Olefins. *RSC Adv.* **2016**, *6*, 22419−22423.

(108) Federsel, C.; Ziebart, C.; Jackstell, R.; Baumann, W.; Beller, M. Catalytic Hydrogenation of Carbon Dioxide and Bicarbonates with a Well-Defined Cobalt Dihydrogen Complex. *Chem. - Eur. J.* **2012**, *18*, 72−75.

(109) Badiei, Y. M.; Wang, W.-H.; Hull, J. F.; Szalda, D. J.; Muckerman, J. T.; Himeda, Y.; Fujita, E. Cp*Co(III) Catalysts with Proton-Responsive Ligands for Carbon Dioxide Hydrogenation in Aqueous Media. *Inorg. Chem.* **2013**, *52*, 12576−12586.

(110) Jeletic, M. S.; Mock, M. T.; Appel, A. M.; Linehan, J. C. A Cobalt-Based Catalyst for the Hydrogenation of CO2 under Ambient Conditions. *J. Am. Chem. Soc.* **2013**, *135*, 11533−11536.

(111) Spentzos, A. Z.; Barnes, C. L.; Bernskoetter, W. H. Effective Pincer Cobalt Precatalysts for Lewis Acid Assisted CO2 Hydrogenation. *Inorg. Chem.* **2016**, *55*, 8225−8233.

(112) Daw, P.; Chakraborty, S.; Leitus, G.; Diskin-Posner, Y.; Ben-David, Y.; Milstein, D. Selective N-Formylation of Amines with H2 and CO2 Catalyzed by Cobalt Pincer Complexes. *ACS Catal.* **2017**, *7*, 2500−2504.

(113) Ge, H.; Jing, Y.; Yang, X. Computational Design of Cobalt Catalysts for Hydrogenation of Carbon Dioxide and Dehydrogenation of Formic Acid. *Inorg. Chem.* **2016**, *55*, 12179−12184.

(114) Bertini, F.; Glatz, M.; Gorgas, N.; Stoger, B.; Peruzzini, M.; Veiros, L. F.; Kirchner, K.; Gonsalvi, L. Carbon Dioxide Hydrogenation Catalysed by Well-defined Mn(I) PNP Pincer Hydride Complexes. *Chem. Sci.* **2017**, *8*, 5024−5029.

(115) Dubey, A.; Nencini, L.; Fayzullin, R. R.; Nervi, C.; Khusnutdinova, J. R. Bio-Inspired Mn(I) Complexes for the Hydrogenation of CO2 to Formate and Formamide. *ACS Catal.* **2017**, *7*, 3864−3868.

(116) Fu, S.; Chen, N.-Y.; Liu, X.; Shao, Z.; Luo, S.-P.; Liu, Q. Ligand-Controlled Cobalt-Catalyzed Transfer Hydrogenation of Alkynes: Stereodivergent Synthesis of Z- and E-Alkenes. *J. Am. Chem. Soc.* **2016**, *138*, 8588−8594.

(117) Landge, V. G.; Pitchaimani, J.; Midya, S. P.; Subaramanian, M.; Madhu, V.; Balaraman, E. Phosphine-free cobalt pincer complex catalyzed Z-selective semi-hydrogenation of unbiased alkynes. *Catal. Sci. Technol.* **2018**, *8*, 428−433.

(118) Yamamoto, A.; Miura, Y.; Ito, T.; Chen, H.-L.; Iri, K.; Ozawa, F. Preparation, X-ray Molecular Structure Determination, and Chemical Properties of Dinitrogen-Coordinated Cobalt Complexes Containing Triphenylphosphine Ligands and Alkali Metal or Magnesium. Protonation of the Coordinated Dinitrogen to Ammonia and Hydrazine. *Organometallics* **1983**, *2*, 1429−1436.

(119) (a) Del Castillo, T. J.; Thompson, N. B.; Suess, D. L. M.; Ung, G.; Peters, J. C. Evaluating Molecular Cobalt Complexes for the Conversion of N_2 to NH_3. *Inorg. Chem.* **2015**, *54*, 9256−9262. (b) Imayoshi, R.; Tanaka, H.; Matsuo, Y.; Yuki, M.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Cobalt-Catalyzed Transformation of Molecular Dinitrogen into Silylamine under Ambient Reaction Conditions. *Chem. - Eur. J.* **2015**, *21*, 8905−8909. (c) Ding, K.; Brennessel, W. W.; Holland, P. L. Three-Coordinate and Four-Coordinate Cobalt Hydride Complexes That React with Dinitrogen. *J. Am. Chem. Soc.* **2009**, *131*, 10804−10805. (d) Rozenel, S. S.; Padilla, R. M.; Arnold, J. Chemistry of Reduced Monomeric and Dimeric Cobalt Complexes Supported by a PNP Pincer Ligand. *Inorg. Chem.* **2013**, *52*, 11544−11550.

(120) Kuriyama, S.; Arashiba, K.; Tanaka, H.; Matsuo, Y.; Nakajima, K.; Yoshizawa, K.; Nishibayashi, Y. Direct Transformation of Molecular Dinitrogen into Ammonia Catalyzed by Cobalt Dinitrogen Complexes Bearing Anionic PNP Pincer Ligands. *Angew. Chem., Int. Ed.* **2016**, *55*, 14291−14295.

(121) Imayoshi, R.; Nakajima, K.; Takaya, J.; Iwasawa, N.; Nishibayashi, Y. Synthesis and Reactivity of Iron− and Cobalt−Dinitrogen Complexes Bearing PSiP-Type Pincer Ligands toward Nitrogen Fixation. *Eur. J. Inorg. Chem.* **2017**, *2017*, 3769−3778.

(122) (a) Godula, K.; Sames, D. C-H Bond Functionalization in Complex Organic Synthesis. *Science* **2006**, *312*, 67−72. (b) Rouquet, G.; Chatani, N. Catalytic Functionalization of C(sp^2)-H and C(sp^3)-H Bonds by Using Bidentate Directing Groups. *Angew. Chem., Int. Ed.* **2013**, *52*, 11726−11743. (c) McMurray, L.; O'Hara, F.; Gaunt, M. Recent Developments in Natural Product Synthesis using Metal-catalysed C−H Bond Functionalization. *Chem. Soc. Rev.* **2011**, *40*, 1885−1898. (d) Gutekunst, W. R.; Baran, P. S. C-H Functionalization Logic in Total Synthesis. *Chem. Soc. Rev.* **2011**, *40*, 1976−1991. (e) Colby, D. A.; Tsai, A. S.; Bergman, R. G.; Ellman, J. A. Rhodium Catalyzed Chelation-Assisted C−H Bond Functionalization Reactions. *Acc. Chem. Res.* **2012**, *45*, 814−825.

(123) Hall, D. G. *Boronic Acids*; Wiley-VCH: Weinheim, Germany, 2005.

(124) (a) Obligacion, J. V.; Semproni, S. P.; Chirik, P. J. Cobalt-Catalyzed C−H Borylation. *J. Am. Chem. Soc.* **2014**, *136*, 4133−4136. (b) Léonard, N. G.; Bezdek, M. J.; Chirik, P. J. Cobalt-Catalyzed C(sp^2)−H Borylation with an Air-Stable, Readily Prepared Terpyridine Cobalt(II) Bis(acetate) Precatalyst. *Organometallics* **2017**, *36*, 142−150.

(125) (a) Schaefer, B. A.; Margulieux, G. W.; Small, B. L.; Chirik, P. J. Evaluation of Cobalt Complexes Bearing Tridentate Pincer Ligands for Catalytic C−H Borylation. *Organometallics* **2015**, *34*, 1307−1320. (b) Obligacion, J. V.; Bezdek, M. J.; Chirik, P. J. C(sp^2)−H Borylation of Fluorinated Arenes Using an Air-Stable Cobalt Precatalyst: Electronically Enhanced Site Selectivity Enables Synthetic Opportunities. *J. Am. Chem. Soc.* **2017**, *139*, 2825−2832. (c) Obligacion, J. V.; Semproni, S. P.; Pappas, I.; Chirik, P. J. Cobalt-Catalyzed C(sp^2)-H Borylation: Mechanistic Insights Inspire Catalyst Design. *J. Am. Chem. Soc.* **2016**, *138*, 10645−10653. (d) Obligacion, J. V.; Chirik, P. J. Mechanistic Studies of Cobalt-Catalyzed C(sp^2)−H Borylation of Five-Membered Heteroarenes with Pinacolborane. *ACS Catal.* **2017**, *7*, 4366−4371.

(126) Ren, H.; Zhou, Y.-P.; Bai, Y.; Cui, C.; Driess, M. Cobalt-Catalyzed Regioselective Borylation of Arenes: N-Heterocyclic Silylene as an Electron Donor in the Metal-Mediated Activation of C−H Bonds. *Chem. - Eur. J.* **2017**, *23*, 5663−5667.

(127) Neely, J. M.; Bezdek, M. J.; Chirik, P. J. Insight into Transmetalation Enables Cobalt-Catalyzed Suzuki−Miyaura Cross Coupling. *ACS Cent. Sci.* **2016**, *2*, 935−942.

(128) Kumar, L. M.; Bhat, B. R. Cobalt Pincer Complex Catalyzed Suzuki-Miyaura Cross Coupling − A Green Approach. *J. Organomet. Chem.* **2017**, *827*, 41−48.

(129) Xiong, Z.; Li, X.; Zhang, S.; Shi, Y.; Sun, H. Synthesis and Reactivity of N-Heterocyclic PSiP Pincer Iron and Cobalt Complexes and Catalytic Application of Cobalt Hydride in Kumada Coupling Reactions. *Organometallics* **2016**, *35*, 357−363.

(130) Qi, X.; Sun, H.; Li, X.; Fuhr, O.; Fenske, D. Synthesis and Catalytic Activity of N-Heterocyclic Silylene (NHSi) Cobalt Hydride for Kumada Coupling Reactions. *Dalton Trans.* **2018**, *47*, 2581−2588.

(131) (a) Donkervoort, J. G.; Vicario, J. L.; Jastrzebski, J. T. B. H.; Cahiez, G.; van Koten, G. Novel Organomanganese(II) Complexes Active as Homogeneous Catalysts in Manganese(II)/copper(I) Catalyzed Carbon-carbon Bond Formation Reactions. *Recl. Trav. Chim. Pays-Bas* **1996**, *115*, 547−548. (b) Donkervoort, J. G.; Vicario, J. L.; Jastrzebski, J. T. B. H.; Gossage, R. A.; Cahiez, G.; van Koten, G. Novel Tridentate Diamino Organomanganese(II) Complexes as Homogeneous Catalysts in Manganese(II)/copper(I) Catalyzed Carbon−carbon Bond Forming Reactions. *J. Organomet. Chem.* **1998**, *558*, 61−69.

(132) Nerush, A.; Vogt, M.; Gellrich, U.; Leitus, G.; Ben-David, Y.; Milstein, D. Template Catalysis by Metal−Ligand Cooperation. C−C Bond Formation via Conjugate Addition of Non-activated Nitriles under Mild, Base-free Conditions Catalyzed by a Manganese Pincer Complex. *J. Am. Chem. Soc.* **2016**, *138*, 6985−6997.

(133) Schmidt, V. A.; Hoyt, J. M.; Margulieux, G. M.; Chirik, P. J. Cobalt-Catalyzed $[2\pi + 2\pi]$ Cycloadditions of Alkenes: Scope, Mechanism, and Elucidation of Electronic Structure of Catalytic Intermediates. *J. Am. Chem. Soc.* **2015**, *137*, 7903−7914.

(134) Langlotz, B. K.; Wadepohl, H.; Gade, L. H. Chiral Bis(pyridylimino)isoindoles: a Highly Modular Class of Pincer Ligands for Enantioselective Catalysis. *Angew. Chem., Int. Ed.* **2008**, *47*, 4670−4674.

(135) Atienza, C. C. H.; Diao, T.; Weller, K. J.; Nye, S. A.; Lewis, K. M.; Delis, J. G. P.; Boyer, J. L.; Roy, A. K.; Chirik, P. J. Bis(imino)pyridine Cobalt-Catalyzed Dehydrogenative Silylation of Alkenes: Scope, Mechanism, and Origins of Selective Allylsilane Formation. *J. Am. Chem. Soc.* **2014**, *136*, 12108−12118.

(136) Scheuermann, M. L.; Semproni, S. P.; Pappas, I.; Chirik, P. J. Carbon Dioxide Hydrosilylation Promoted by Cobalt Pincer Complexes. *Inorg. Chem.* **2014**, *53*, 9463−9465.

(137) Schuster, C. H.; Diao, T.; Pappas, I.; Chirik, P. J. Bench-Stable, Substrate-Activated Cobalt Carboxylate Pre-Catalysts for Alkene Hydrosilylation with Tertiary Silanes. *ACS Catal.* **2016**, *6*, 2632−2636.

(138) Du, X.; Hou, W.; Zhang, Y.; Huang, Z. Pincer Cobalt Complex-catalyzed Z-selective Hydrosilylation of Terminal Alkynes. *Org. Chem. Front.* **2017**, *4*, 1517−1521.

(139) Zhou, H.; Sun, H.; Zhang, S.; Li, X. Synthesis and Reactivity of a Hydrido CNC Pincer Cobalt(III) Complex and Its Application in Hydrosilylation of Aldehydes and Ketones. *Organometallics* **2015**, *34*, 1479−1486.

(140) Sauer, D. C.; Wadepohl, H.; Gade, L. H. Cobalt Alkyl Complexes of a New Family of Chiral 1,3-Bis(2-pyridylimino)-isoindolates and Their Application in Asymmetric Hydrosilylation. *Inorg. Chem.* **2012**, *51*, 12948−12958.

(141) (a) Cheng, B.; Lu, P.; Zhang, H.; Cheng, X.; Lu, Z. Highly Enantioselective Cobalt-Catalyzed Hydrosilylation of Alkenes. *J. Am. Chem. Soc.* **2017**, *139*, 9439−9442. (b) Guo, J.; Lu, Z. Highly Chemo-, Regio-, and Stereoselective Cobalt-Catalyzed Markovnikov Hydrosilylation of Alkynes. *Angew. Chem., Int. Ed.* **2016**, *55*, 10835−10838.

(142) Mukhopadhyay, T. K.; Flores, M.; Groy, T. L.; Trovitch, R. J. A Highly Active Manganese Precatalyst for the Hydrosilylation of Ketones and Esters. *J. Am. Chem. Soc.* **2014**, *136*, 882−885.

(143) (a) Obligacion, J. V.; Chirik, P. J. Bis(imino)pyridine Cobalt-Catalyzed Alkene Isomerization−Hydroboration: A Strategy for Remote Hydrofunctionalization with Terminal Selectivity. *J. Am. Chem. Soc.* **2013**, *135*, 19107−19110. (b) Obligacion, J. V.; Neely, J. M.; Yazdani, A. N.; Pappas, I.; Chirik, P. J. Cobalt Catalyzed *Z*-Selective Hydroboration of Terminal Alkynes and Elucidation of the Origin of Selectivity. *J. Am. Chem. Soc.* **2015**, *137*, 5855−5858.

(144) Zhang, L.; Zuo, Z.; Leng, X.; Huang, Z. A Cobalt-Catalyzed Alkene Hydroboration with Pinacolborane. *Angew. Chem., Int. Ed.* **2014**, *53*, 2696−2700.

(145) Xi, T.; Lu, Z. Cobalt-Catalyzed Ligand-Controlled Regioselective Hydroboration/ Cyclization of 1,6-Enynes. *ACS Catal.* **2017**, *7*, 1181−1185.

(146) Guo, J.; Cheng, B.; Shen, X.; Lu, Z. Cobalt-Catalyzed Asymmetric Sequential Hydroboration/Hydrogenation of Internal Alkynes. *J. Am. Chem. Soc.* **2017**, *139*, 15316−15319.

(147) Zhang, G.; Zeng, H.; Wu, J.; Yin, Z.; Zheng, S.; Fettinger, J. C. Highly Selective Hydroboration of Alkenes, Ketones and Aldehydes Catalyzed by a Well-Defined Manganese Complex. *Angew. Chem., Int. Ed.* **2016**, *55*, 14369−14372.

(148) Vasilenko, V.; Blasius, C. K.; Wadepohl, H.; Gade, L. H. Mechanism-Based Enantiodivergence in Manganese Reduction Catalysis: A Chiral Pincer Complex for the Highly Enantioselective Hydroboration of Ketones. *Angew. Chem., Int. Ed.* **2017**, *56*, 8393−8397.

(149) Small, B. L.; Brookhart, M.; Bennett, A. M. A. Highly Active Iron and Cobalt Catalysts for the Polymerization of Ethylene. *J. Am. Chem. Soc.* **1998**, *120*, 4049−4050.

(150) (a) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. Novel Olefin Polymerization Catalysts Based on Iron and Cobalt. *Chem. Commun.* **1998**, 849−850. (b) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Stroemberg, S.; White, A. J. P.; Williams, D. J. Iron and Cobalt Ethylene Polymerization Catalysts Bearing 2,6-Bis(Imino)Pyridyl Ligands: Synthesis, Structures, and Polymerization Studies. *J. Am. Chem. Soc.* **1999**, *121*, 8728−8740.

(151) Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci, F.; Zanobini, F.; Laschi, F.; Sommazzi, A. Oligomerisation of Ethylene to Linear α-Olefins by new C_s- and C_1-Symmetric [2,6-Bis(imino)pyridyl]iron and -cobalt Dichloride Complexes. *Eur. J. Inorg. Chem.* **2003**, *2003*, 1620−1631.

(152) Al Thagfi, J.; Lavoie, G. G. Synthesis, Characterization, and Ethylene Polymerization Studies of Chromium, Iron, and Cobalt Complexes Containing 1,3-Bis(imino)-N-Heterocyclic Carbene Ligands. *Organometallics* **2012**, *31*, 2463−2469.

(153) Gong, D.; Zhang, X.; Huang, K.-W. Regio- and Stereoselective Polymerization of 1,3-Butadiene Catalyzed by Phosphorus−nitrogen PN^3-pincer Cobalt(II) Complexes. *Dalton Trans.* **2016**, *45*, 19399−19407.