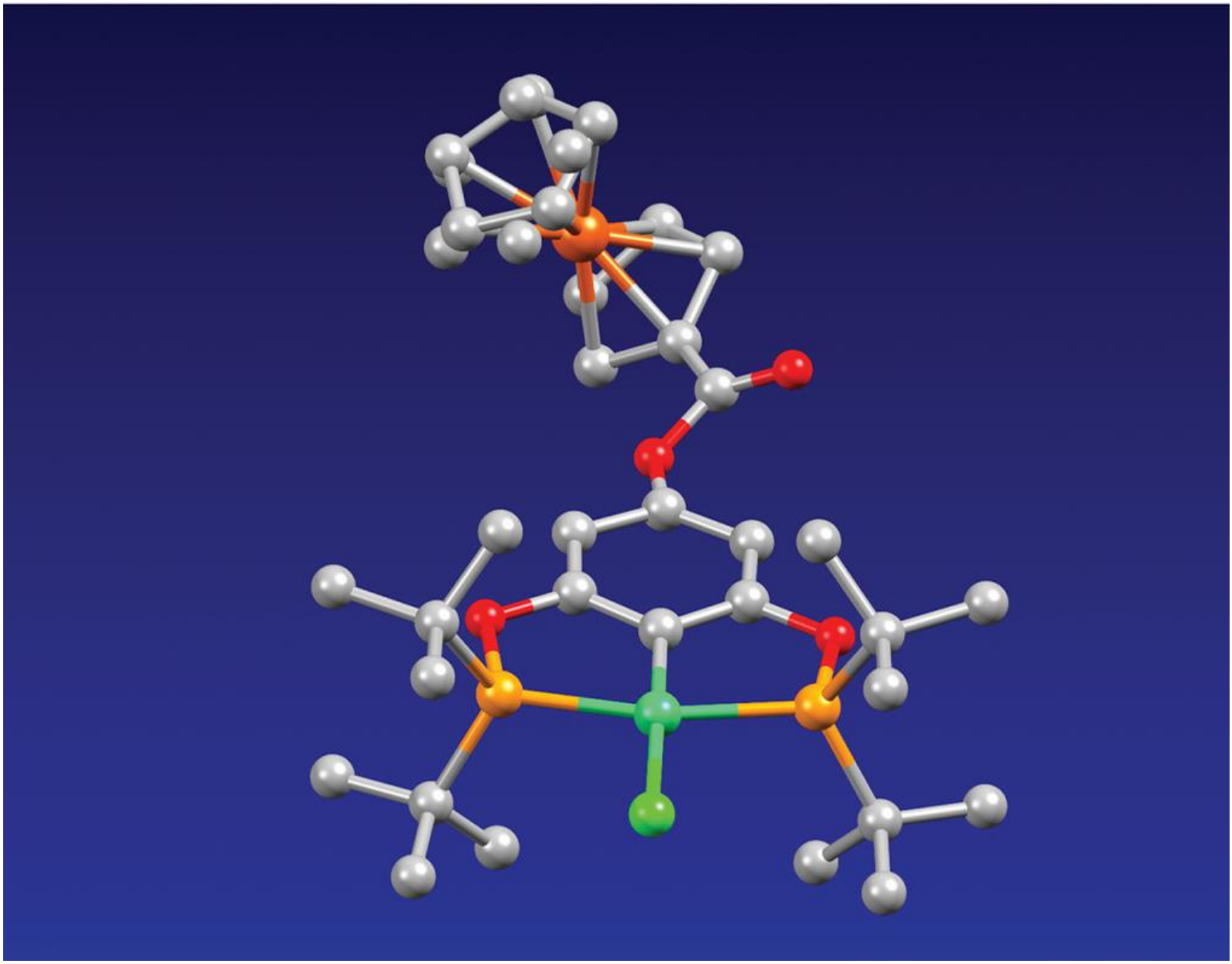
Pincer Compounds

Chemistry and Applications

Edited by David Morales-Morales



Chapter 24

Chemistry of Mn and Co Pincer Compounds

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Chapter Outline

24.1 Introduction **491**
24.2 Manganese Pincers **491**
24.2.1 Dehydrogenation of Alcohols 491
24.2.2 Dehydrogenative Coupling of Alcohols 492
24.2.3 Dehydrogenative Coupling of Alcohols and Amines 492
24.2.4 Dehydrogenative Deoxygenation of Primary Alcohols 495
24.2.5 Heterocycle Synthesis 495
24.2.6 Aminomethylation 496
24.2.7 Decomposition of Formic Acid 496
24.2.8 α-Alkylation of Ketones 497
24.2.9 Transfer Hydrogenation of Ketones 497
24.2.10 Hydrogenation of Nitriles, Ketones, and Aldehydes 498
24.2.11 Hydrogenation of Amides 499
24.2.12 Hydrogenation of Esters 499
24.2.13 Hydroboration of Alkenes, Ketones and Aldehydes 500
24.2.14 Michael Addition Reaction of Aliphatic Nitriles to α,β-Unsaturated Carbonyl Compounds 501
24.2.15 Electrocatalytic Oxidation of Hydrogen 501
24.2.16 Homo-Coupling of Aryl Grignard Reagents 502
24.3 Cobalt Pincers **502**
24.3.1 Ketone and Imine Hydrogenation/Dehydrogenation 502
24.3.2 Alkene Hydrogenation 504
24.3.3 Alkene Polymerization and Cycloaddition 506
24.3.4 Alkene Hydrosilation 507
24.3.5 Alkene Hydroboration 507
24.3.6 Alkyne Hydroboration 509
24.3.7 Arene Hydroboration 509
24.3.8 Reactions With CO_2 511
24.3.9 Miscellaneous Reactions of Cobalt Pincer Complexes 512
24.4 Recent Additions **514**
References **516**

24.1 INTRODUCTION

Since the publication of the first edition of this book on pincer chemistry in 2007, many reports have been made of PCP, PNP, and NNN ligands on first row metals. In this chapter, we look at examples of manganese and cobalt pincer complexes and the types of reaction for which they have found use. Four common classes of pincer ligand are found. Perhaps the simplest is the $N(CH_2CH_2PR_2)_2$ type ligand, where R is typically i-propyl or t-butyl. A well-established ligand is the PCP bis(phosphino)phenyl ligand $R_2PCH_2C_6H_3CH_2PR_2$, and is pyridine analog (PNP). Finally, extensive studies have appeared using the pyridinediimine (PDI) ligand, $RN = 2,6\text{-}(CH = NR)_2NC_5H_3$. Many of these ligands have been found to be active in "non-innocent" behavior, in that the ligand can change its donor properties (X vs L type ligand [1]). These complexes serve as catalyst (precursors) for a variety of different addition and functionalization reactions. Below, the complexes and their reactivities are sorted on the basis of the type of reaction they exhibit.

24.2 MANGANESE PINCERS

24.2.1 Dehydrogenation of Alcohols

Beller et al. [2] reported structurally defined manganese pincer complexes **1** and **2**, which can promote the selective dehydrogenation of aqueous methanol under basic conditions (Eq. 24.1). The catalyst **1** exhibited an impressive

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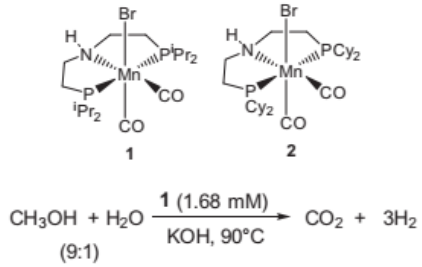
long-term stability (about a month) and turnover number (TON) >20,000. A manganese methoxide species formed during the reaction was identified as a key intermediate, which then forms an aldehyde with the subsequent release of hydrogen as driven by the cooperativity of the ligand-metal framework. Other important hydrogen carriers, such as ethanol, paraformaldehyde, and formic acid, were also dehydrogenated successfully attaining TONs of 163, 79, and 283 respectively in 5 h.



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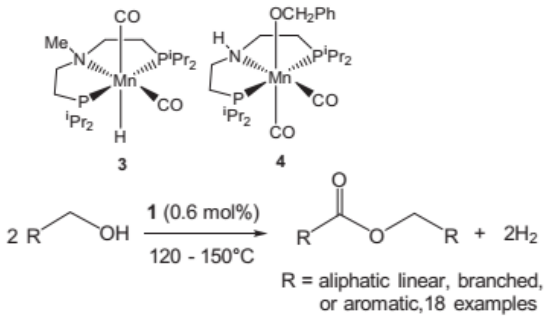
24.2.2 Dehydrogenative Coupling of Alcohols

Gauvin et al. [3] demonstrated the utility of the same PNP pincer-supported manganese(I) dicarbonyl complex **1** in the acceptorless dehydrogenative coupling of variety of aliphatic and benzylic alcohols to produce the corresponding esters under base-free conditions (Eq. 24.2). The higher linear alcohols were converted into the corresponding esters in good yields (76%−83%) at 150°C, within 24 h, whereas lighter alcohols took more time (72 h) in order to achieve similar conversions at 120°C. Due to steric effects, branched aliphatic alcohols suffer low conversions. The mechanistic details of the process were revealed by both experimental and density functional theory (DFT) studies. Cooperativity of the metal − ligand framework was found to be crucial in this catalytic cycle and the N-methylated counterpart **3** was inactive. It was seen that addition of water or methanol did not affect the activity of the catalysts, but potassium bromide or butyric acid inhibited the reaction significantly. The alkoxide moiety **4**, which is one of the key intermediates, was isolated and characterized. As per the calculations, in this case of manganese catalyzed reactions, dehydrogenation of the substrate into aldehyde is more energy-demanding as compared to the hydrogen release from the metal−ligand cooperative system.



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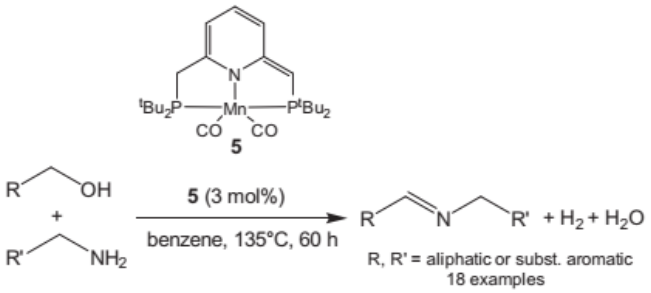
24.2.3 Dehydrogenative Coupling of Alcohols and Amines

Earlier in 2016, Milstein et al. [4] employed a pyridine-based PNP manganese pincer catalyst **5** in the catalytic dehydrogenative coupling of alcohols and amines to form aldimines (Eq. 24.3). A variety of substituted benzyl alcohols were coupled with amines containing either electron-donating or -withdrawing substituents under neutral conditions (conversions 42%−99%). Amines bearing electron-donating substituents provided higher yields compared to the electron withdrawing versions due to their high nucleophilicity. On the other hand, the linear aliphatic substrates (both amine and alcohol) react slowly compared to the cyclic aliphatic or aromatic substrates. The presence of the liberated H_2 in the reaction vessel did not seem to affect the reaction. The mechanistic details of the catalytic reaction were established by infra-red (IR) and nuclear magnetic resonance (NMR) studies, stoichiometric reactions, and isolation of intermediates. The reaction was proposed to proceed through a concerted, bifunctional proton and hydride transfer pathway; the formation of an aldehyde by the direct β-H elimination of the alkoxy ligand was not considered.



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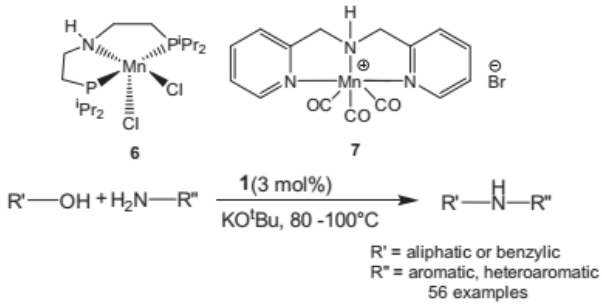
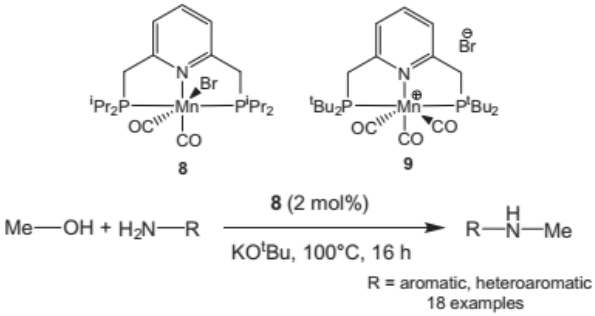
Beller et al. [5] used their stable manganese pincer catalysts **1** and **2** in the formation of intra- or intermolecular C−N bonds by adapting the "hydrogen borrowing" strategy. N-alkylation of a variety of (hetero) aromatic amines by primary alcohols (aliphatic or benzylic) was achieved under basic, mild conditions (80−100°C), mostly in quantitative yields, while maintaining an excellent chemoselectivity (Eq. 24.4). The catalytic system was found to be compatible with various, sensitive, reducible functional groups, including olefins, halides, thioether, benzodioxane, and heteroaromatic groups. Especially, it can efficiently promote chemoselective monomethylation of primary amines using methanol under mild conditions. But in this particular case, the olefin and iodide containing substrates suffered side reactions. The related manganese(II) PNP pincer complex **6** and the cationic Mn(I) NNN pincer complex **7** were found to be less active for these N-alkylation reactions.



(24.4)

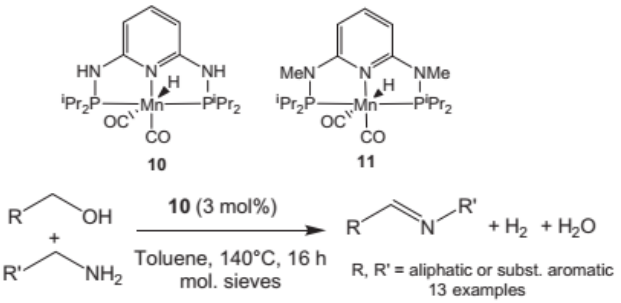
Beller [6] later reported that a new lutidine-based manganese PNP-pincer complex **8** is a better catalyst for the selective N-methylation of aromatic amines with methanol compared to their previously reported system employing **1**. With this new system they could selectively monomethylate various aromatic amines under milder conditions in high yields (up to 99%) (Eq. 24.5). Ortho-substituted anilines provided lower yields compared to the *meta*- and *para*-substituted versions due to the steric constraints. A high tolerance toward functional groups, such as ketones, C = C double bonds, or amides, was observed; however, nitrile substituted anilines were found to be incompatible with this system under the optimized reaction conditions. In the case of ortho-substituted aniline derivatives, the desired products were obtained in moderate yields. The structurally related complex **9** was found to be completely inactive in the catalytic reaction under optimized reaction conditions, indicating the key role of phosphorus substituents on the catalysis (Eq. 24.5).



(24.5)

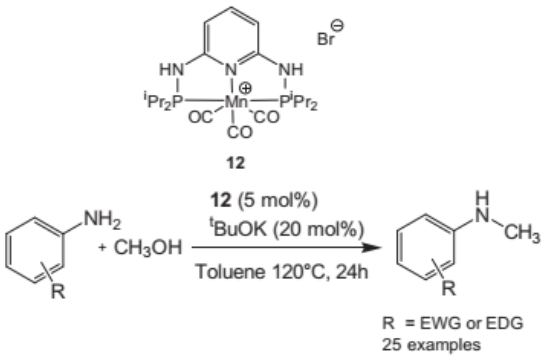
Kirchner et al. [7] employed their new PNNNP pincer manganese hydride catalyst **10** in the same reaction, and were able to convert a range of alcohols and amines including both aromatic and aliphatic substrates into the corresponding imines selectively in good to excellent yields (60%−92%) under base free conditions (Eq. 24.6). Lewis acidic additives like 3 Å molecular sieves or LiOTf were found to play a key role in achieving good conversions. In the reaction of ^{n}BuOH and *p*-toluidine, a small amount (17%) of the desired free imine was obtained, while the rest of the product

undergoes polymerization. The N-methylated complex **11** was found to be inactive in the catalytic reactions, which indicates the importance of NH functionalities in the reaction. DFT calculations performed by probing ethanol as the model substrate indicated a concerted mechanism for the dehydrogenation step similar to the mechanism proposed by Milstein [4]. The overall reaction barrier (33 kcal/mol) calculated was in accordance with the required reaction temperature (140°C), and the driving force for the reaction was provided by the sequential condensation between aldehyde and amine and removal of water by molecular sieves.



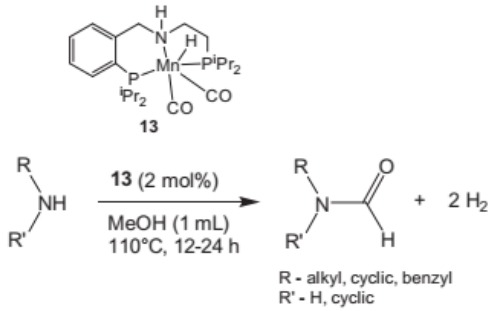
(24.6)

Sortais et al. [8] demonstrated the applicability of a cationic PNNNP manganese catalyst **12** in the selective methylation of aniline derivatives with methanol (yields 60%–99%) (Eq. 24.7). This system was found to operate in presence of a catalytic amount of base (20 mol%) and tolerates a large scope of functional groups such as nitro, cyano, acetyl, acetal, ester, and primary amide groups. Sulfonamides were also methylated in excellent yields under harsher conditions (1.2 equiv of base for 60 h). However, the presence of an acidic phenol functionality or the steric hindrance of substituents was found to inhibit the reactions. From the stoichiometric and NMR studies it was established that a manganese hydride species was formed during the reaction and an excess of base (20 mol%) was required to stabilize or reactivate the active species during the reaction.



(24.7)

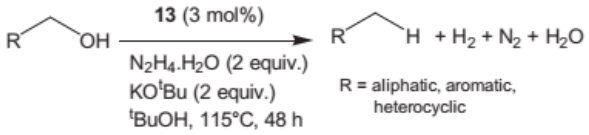
Recently Milstein [9] developed a manganese pincer system **13** that can promote the N-formylation of amines by the dehydrogenative coupling of methanol under homogeneous, mild reaction conditions without the help of any additives (Eq. 24.8). A variety of amines were converted into their respective N-formylated products in good yields (53%–86%); however, a noticeable amount of N-methylated side products were also observed, resulting from a "borrowed hydrogen" route. Mechanistic studies revealed the formation of an alkoxy intermediate in the reaction and the catalytic cycle involves activation of O–H by amido-amine metal–ligand cooperation. The participation of the benzylic group in H_2 liberation was ruled out by DFT calculations.



(24.8)

24.2.4 Dehydrogenative Deoxygenation of Primary Alcohols

Milstein's new catalyst **13** was also found to be very useful in the catalytic deoxygenation of benzylic and aliphatic primary alcohols through an oxidative dehydrogenation/Wolff − Kishner reduction pathway [10]. Excellent yields were observed in the case of primary benzylic and aliphatic alcohols (80%−99%) but secondary alcohols gave low conversions (Eq. 24.9). The system exhibited a high tolerance toward various reactive functionalities in the substrates including the $-NH_2$ group, but often hydrogenated C = C double bonds. The hydrozone motif formed by the dehydrogenative coupling of the alcohol was found to be the key intermediate in the process, which upon a base mediated Wolff − Kishner reduction led to the deoxygenated product.



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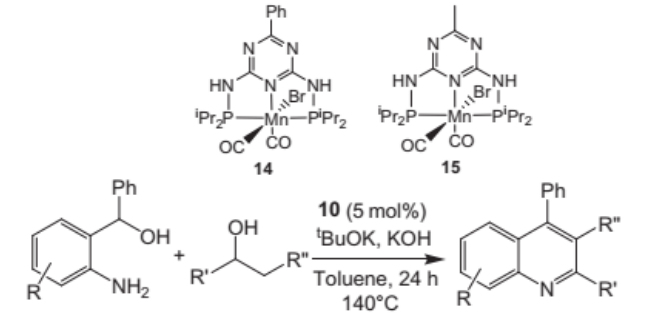
24.2.5 Heterocycle Synthesis

Kirchner [11] exploited the profound alcohol dehydrogenating ability of the PNNNP manganese hydride complex **10** by employing it in the catalytic synthesis of substituted quinolones and pyrimidines. Quinolines were obtained by the combination of 2-aminobenzyl alcohols with a secondary alcohol (yield, up to 91%) (Eq. 24.10), and the pyrimidine derivatives were obtained by a three component synthesis using benzamidine, primary, and secondary alcohols (yield, up to 90%) (Eq. 24.11). Both of these reactions proceeded through the acceptorless dehydrogenation of alcohols followed by the selective formation of C − C and C − N bonds upon condensation. The presence of excess base and a cooperative N−H functionality on the ligand backbone were found to be key for the catalytic activity; catalyst **11** bearing N−Me linkers was found to be catalytically inactive. The PNNNP manganese complexes **14** and **15**, featuring a triazine backbone instead of a pyridine ring, were found to be less active in this reaction.



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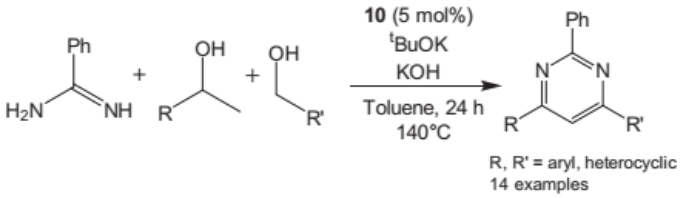
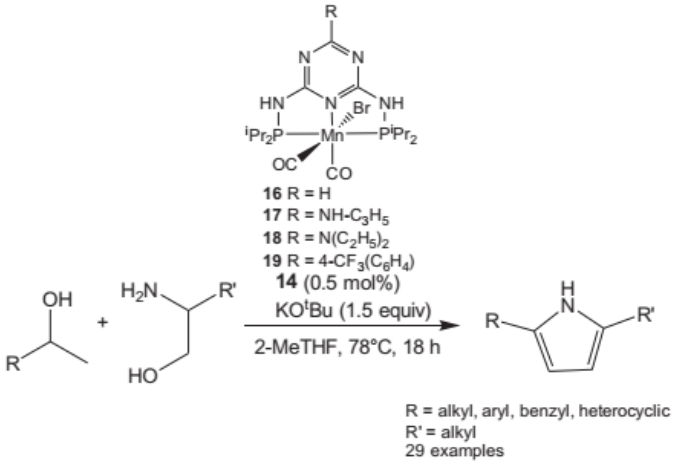


(24.11)

Recently, Kempe [12] showed that triazine-based PNNNP manganese complex **14** developed by Kirchner is an excellent catalyst for the synthesis of pyrroles from secondary alcohols and amino alcohols providing good to excellent yields under mild reaction conditions (Eq. 24.12). The reaction was proposed to proceed through dehydrogenation of both alcohol and amino alcohol in the presence of base followed by the formation of the corresponding imine intermediate, and then the desired pyrroles upon cyclization with the help of base. The balance between the rate of dehydrogenation of substrate and reagent was found to be important in order to minimize side-product formation and to ensure a high yield of pyrroles. The related complexes with different substitutions on the triazine backbone (**15**−**19**) were found to be relatively less active.



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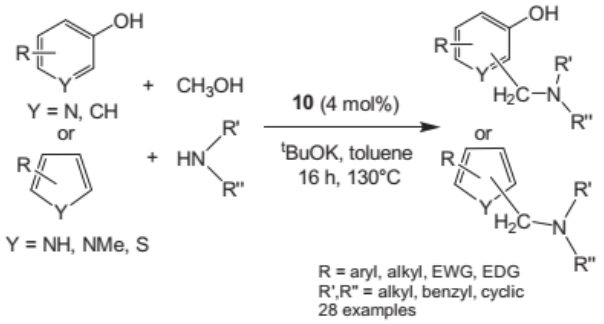
24.2.6 Aminomethylation

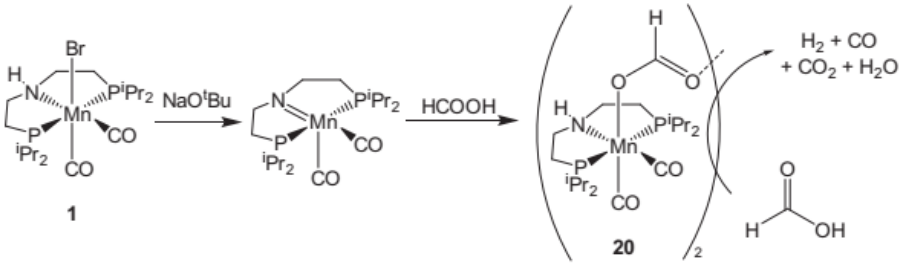
Kirchner et al. [13] recently showed that their system **10** can effectively and selectively promote aminomethylation of various activated aromatic and heteroaromatic substrates using a secondary amine and methanol under mild reaction conditions (isolated yields of up to 91%). No evidence for methylation was observed, which is in contrast to the related isoelectronic Fe(II) catalyst, which gave mainly the methylated products under similar conditions (Eq. 24.13). In the case of carbazole and indole, aminomethylation was observed at the nitrogen site instead of the regular C-position, while reaction of 1-methylindole with imidazole resulted in dimerization. This selective C−C and C−N bond formation reaction was proposed to proceed through a sequence of dehydrogenation and condensation steps, releasing hydrogen and water as byproducts. However, detailed mechanistic studies were not deployed.



(24.13)

24.2.7 Decomposition of Formic Acid

PNP pincer manganese formate **20** was prepared by Boncella et al. [14] by the 1,2-addition of formic acid to the dehydrohalogenated version of the manganese pincer complex **1** (Eq. 24.14). The dimeric manganese formate complex **20** was found to decompose formic acid catalytically under dilute conditions. By the product analysis, which contain H_2, CO, CO_2, and H_2O, the presence of both dehydrogenation and dehydration pathways under the catalytic conditions were recognized. However, this report lacked studies that are needed to understand the mechanistic details of the catalytic reaction and the strong inhibitory effect caused by $LiBF_4$.



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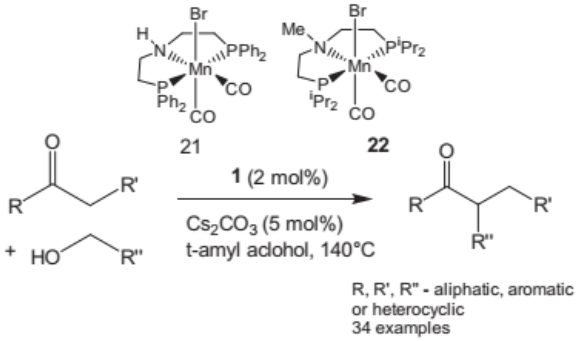
24.2.8 α-Alkylation of Ketones

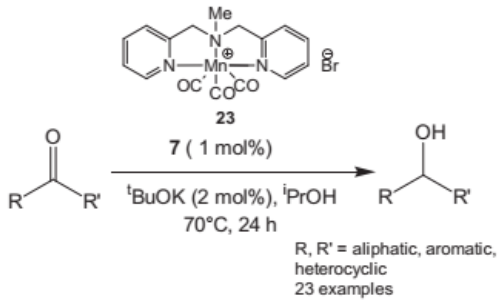
Using a hydrogen autotransfer strategy, Beller [15] developed a manganese-mediated catalytic protocol for the α-alkylation of ketones by primary alcohols in the presence of a base. Ligand–metal cooperativity exhibited by the PNP manganese complex **1** facilitated the functionalization of a broad range of valuable ketones, including 2-oxindole, estrone 3-methyl ether, and testosterone (Eq. 24.15). Under optimized conditions, substrates with electron-withdrawing substituents showed lower conversions as compared to those with electron-donating substituents. The aliphatic and heteroaromatic substrates also exhibited comparatively lower conversions. Complex **1** was found to be a better catalyst as compared to complex **2** and **21** in this process. Detailed mechanistic investigations of the catalytic reactions suggested an intramolecular amidate-assisted alcohol-dehydrogenation pathway. However, catalytic activity exhibited by the N-methylated complex **22** and deuterium-labeling experiments indicated the possibility of different pathways along with the NH-assisted outer-sphere mechanism.



(24.15)

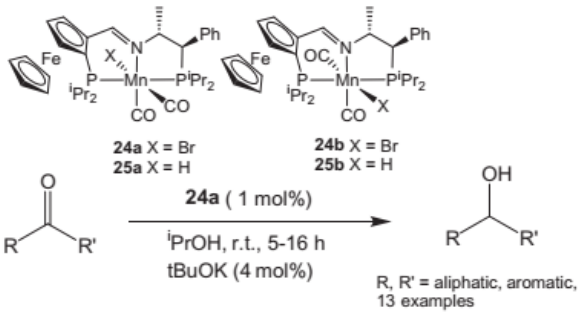
24.2.9 Transfer Hydrogenation of Ketones

A well-defined manganese *N*,*N*,*N*-pincer catalyst **7** was employed by Beller [16] in the transfer hydrogenation of a wide range of ketones providing the corresponding secondary alcohols under basic conditions (Eq. 24.16). Aromatic substrates with electron withdrawing substituents provided higher conversions than those with electron-donating substituents, while cyclic aliphatic ketones provide higher yields than their linear chain counterparts. In the case of heteroaromatic ketones, higher catalyst loading was needed to get better conversions. No products were obtained in the case of aldehydes. From the deuterium labeling experiments, the possibility of a monohydride-based concerted or stepwise mechanism was proposed; however, the comparable reactivity exhibited by the N-methylated catalyst **23** suggested that direct ligand cooperativity with the metal center might not be mandatory in this case to achieve good conversions.



(24.16)

Novel manganese complexes containing a tridentate ligand with a planar chiral ferrocene and a central chiral aliphatic unit **24ab** and **25ab** were employed in the enantioselective transfer hydrogenations of ketones by the Kirchner group [17]. Conversions up to 96% with about 86% e.e. values were reported (Eq. 24.17). The added H_2 did not affect the catalytic conversions or the selectivity, indicating that only the transfer hydrogenation route is operative in this process. Hydride complexes **25ab** catalyzed the reactions relatively faster than the bromide complexes **24ab**, but still entailed the same amount of base (4 equiv). From mechanistic experiments and calculations, an outer-sphere hydrogen transfer pathway for the catalytic reaction was proposed with the key formation of a manganese hydride complex. The higher selectivity observed was correlated to the steric features of the catalyst and the possible hydrogen bonding between the ligand and the oxygen atom of the substrates.



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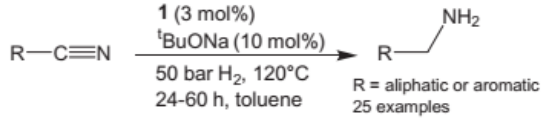
24.2.10 Hydrogenation of Nitriles, Ketones, and Aldehydes

PNP manganese pincer complex **1** developed by Beller was found to be a very efficient and selective hydrogenation catalyst for a variety of substrates including aromatic and aliphatic nitriles, ketones, and aldehydes under optimized conditions [18]. Various electron-donating and -withdrawing substituents, sensitive functionalities such as amines, esters, lactams, and isolated C = C bonds as well as heterocycles were tolerated (Eqs. 24.18, 24.19, 24.20). On the basis of mechanistic studies composed of both experiments and calculations they proposed an outer-sphere mechanism for this homogenous catalytic process that involves a simultaneous transfer of a hydride from the Mn center (Mn − H) and a proton from the nitrogen (N − H) to the substrate. The manganese hydride complex **26** synthesized by the independent route exhibited slightly lower activity attributed to its lower stability.



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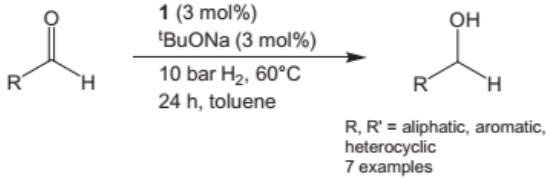

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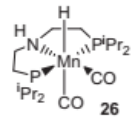
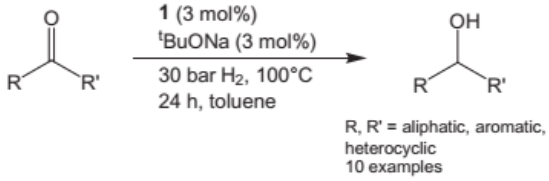
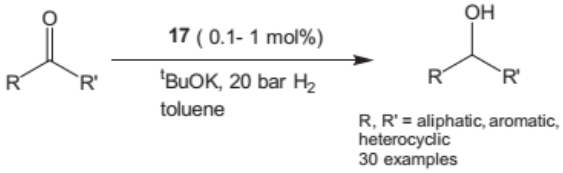




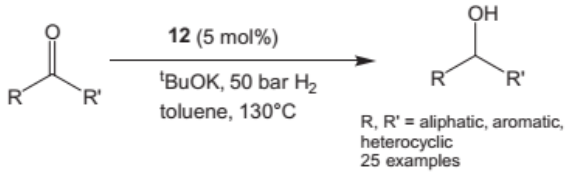
(24.20)

Kempe [19] employed his PNNNP manganese pincer complexes **14–18** in C = O bond hydrogenation chemistry. Catalyst **17** was found to be the best among the catalysts used. It was able to selectively hydrogenate various ketones including aryl–alkyl, diaryl, dialkyl, and cycloalkyl ketones as well as aldehydes (Eq. 24.21). It exhibited outstanding functional group tolerance even to a nonshielded olefin group. This study also emphasized the importance of fine tuning of the structural features of the catalyst in order to achieve better catalytic activity.



(24.21)

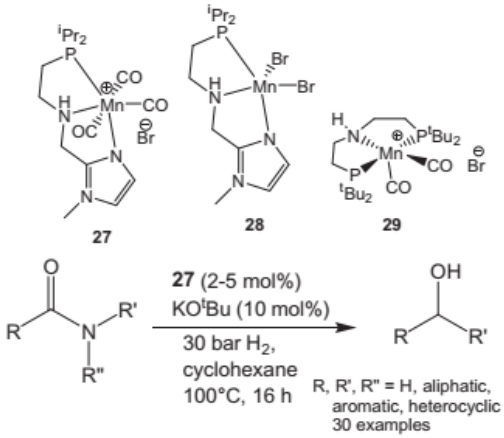
Sortais et al. [20] employed their diaminopyridinyldiphosphine-based manganese pincer catalyst **12** in the hydrogenation of various ketones under 50 bar of H_2 at 130°C to obtain the corresponding alcohols (Eq. 24.22). Compared to the Beller [16] and Kempe [17] systems, this catalyst exhibited lower catalytic activity and required higher catalyst loadings; however, a variety of functional groups including electron-withdrawing or -donating groups and heterocycles were well tolerated. Furthermore, this system was found to efficiently catalyze the reverse reaction, dehydrogenation/oxidation of alcohol to the corresponding ketone.



(24.22)

24.2.11 Hydrogenation of Amides

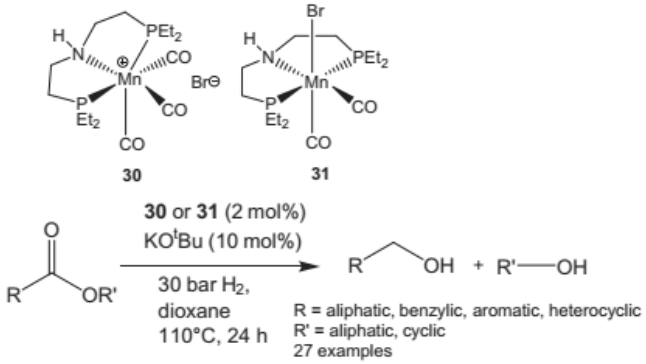
Beller et al. [21] developed a new NNP manganese pincer complex, **27**, for the selective hydrogenation of a wide range of secondary and tertiary amides under mild reaction conditions. They showed that, with their system, primary aromatic amides can also be hydrogenated into the corresponding amines and alcohols (Eq. 24.23). This catalyst has shown excellent selectivity even in the presence of other reducible groups like carbamate or urea. However, this system failed to hydrogenate the aliphatic N-alkyl amides or nonactivated N-alkyl substituted benzamides. Base was found to be necessary for this system to be active, which suggested the formation of the amido complex as a likely active species during the reaction. The outer-sphere catalytic cycle (similar to the hydrogenation of ketones) by these types of the pincer catalysts was proposed. Closely related PNN Mn(II) complex **28** and a PNP Mn(I) complex **29** were found to be inactive in this process.



(24.23)

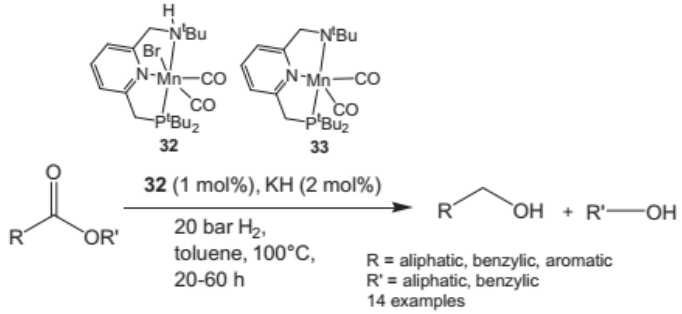
24.2.12 Hydrogenation of Esters

The first manganese-catalyzed hydrogenation of esters to obtain alcohols was reported by the Beller group [22]. A cationic PNP manganese pincer catalyst, **30**, was found to be an excellent catalyst for the effective and selective hydrogenation of esters. Various aromatic esters containing electron-donating, electron-withdrawing, bulky, or heteroaromatic substituents along with aliphatic esters, diesters, and lactones were hydrogenated selectively to the corresponding alcohols in moderate to good yields (78%–95%) (Eq. 24.24). However, with some substrates, such as methyl cinnamate, saturation of the double bond was also observed. The neutral complex **31** formed the same active species under the reaction conditions and exhibited the same activity. The other PNP manganese pincer complexes **1** and **2** were found to be poorly active in this reaction. From the mechanistic data and DFT calculations, an outer-sphere mechanism involving a manganese hydride intermediate was proposed.



(24.24)

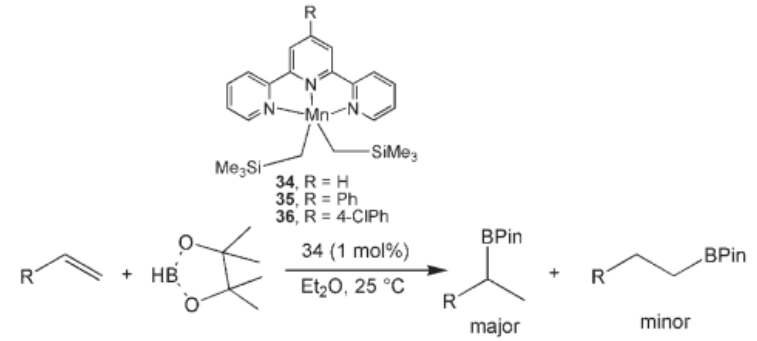
Milstein et al. [23] employed their PNN manganese pincer catalyst **32** in the hydrogenation of esters. This catalyst exhibited excellent activity even with the lower catalyst (1 mol%) and base (KH, 2 mol%) loadings as compared to the Beller's system (**30**) but required longer reaction times depending on the substrate (Eq. 24.25). This system was also found to be selective toward the hydrogenation of an ester group even in the presence of double bond or nitrile functionalities. The proposed intermediate of the catalytic reaction, manganese hydride complex **33** synthesized by the dehydrohalogenation of complex **32**, exhibited similar catalytic activity in the absence of a base, confirming its existence in the actual catalytic reaction. Deprotonation of the benzylic position was not observed in the NMR studies, and H_2 activation was proposed to take place through metal–ligand cooperation.



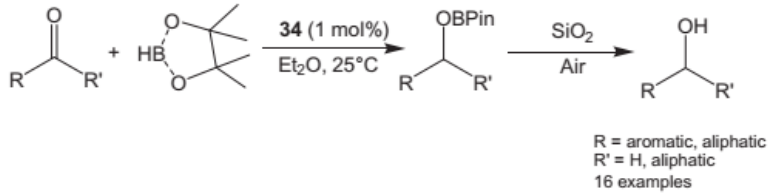
(24.25)

24.2.13 Hydroboration of Alkenes, Ketones and Aldehydes

Terpyridine-based NNN manganese pincer complexes developed by Zhang et al. [24] were found to be highly effective as well as regio- and chemoselective hydroboration catalysts for a range of alkenes, ketones, and aldehydes. Highly Markovnikov regioselective hydroboration of styrenes (as high as 95:5) and chemoselective hydroboration of ketones over alkenes by a manganese catalyst were achieved using **34** (1 mol%) under mild, homogeneous conditions. Catalysts having a different functional group on the ligand backbone, **35** and **36**, exhibited poor conversions but the regioselectivity was kept high. Both electron-donating and electron-withdrawing groups on the styrene were found to be compatible, but nitro, cyano, and alkenyl groups were not tolerated. In the case of aliphatic alkenes, the conversions and regioselectivity were found to be inferior to those for aromatic alkenes (Eq. 24.26). Ketones and aldehydes were also hydroborated in excellent yields (Eq. 24.27). Excellent tolerance and activity toward a variety of electron-donating or -withdrawing groups was observed. In the case of cyclopropyl phenyl ketone no ring-opening products were observed, indicating the noninvolvement of a radical intermediate. In substrates containing both C = C and C = O bonds, such as trans-cinnamaldehyde, hydroboration selectively occurred on the C = O bond even in the presence of excess borane reagent, indicating the chemoselectivity of ketones over alkenes for this manganese-catalyzed hydroboration reaction.



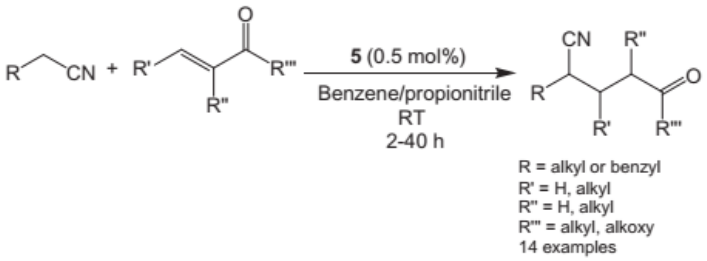
(24.26)



(24.27)

24.2.14 Michael Addition Reaction of Aliphatic Nitriles to α,β-Unsaturated Carbonyl Compounds

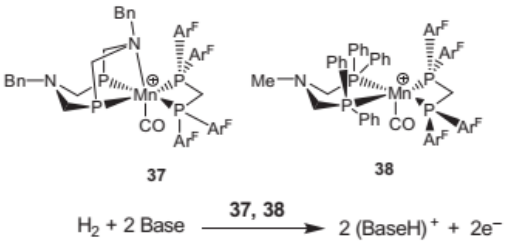
Milstein's catalyst **5** was found to promote the catalytic Michael addition of nonactivated aliphatic nitriles to the α,β-unsaturated carbonyl compounds under mild, neutral conditions [25]. The catalytic system tolerates a variety of nitriles and Michael acceptors with different steric features and acceptor strengths and provides good to excellent yields (40%–93%) (Eq. 24.28). From the NMR spectroscopic investigations and DFT calculations, a reaction mechanism involving a cooperative activation of alkyl nitriles, followed by the formation of a key α-cyano carbanion analog was established. The metal center was believed to promote the catalysis indirectly by cooperating with the ligand leading to the template catalysis.



(24.28)

24.2.15 Electrocatalytic Oxidation of Hydrogen

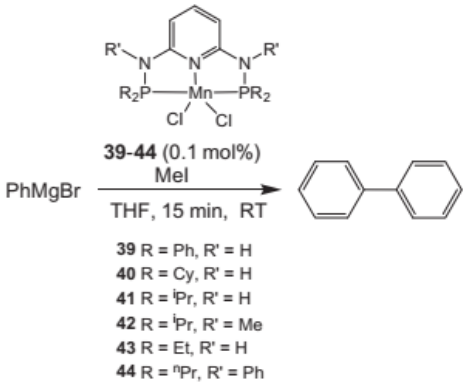
Bullock [26] developed manganese complexes **37** and **38** that can electrocatalyze the oxidation of H_2 at 1 atm (Eq. 24.29). Catalyst **37**, in fluorobenzene with 2,6-lutidine as the exogeneous base, exhibits best reactivity with a turnover frequency (TOF) of 3.5 s^{-1} with an estimated overpotential of 700 mV. Catalyst **38**, in fluorobenzene along with N-methylpyrrolidine as the exogeneous base, exhibits a TOF of 1.4 s^{-1} with an estimated overpotential of 880 mV. From computational studies it was shown that the slow intramolecular deprotonation of the manganese hydride species by the pendent amine (outer-sphere mechanism) limits the rate of the electrocatalytic oxidation of H_2.



(24.29)

24.2.16 Homo-Coupling of Aryl Grignard Reagents

Kirchner [27] synthesized a series of PNP manganese pincer complexes **39–44**, and employed them in a catalytic oxidative homocoupling of aryl Grignard reagents in the presence of MeI as oxidizing agent to obtain symmetrical biaryls in good to excellent isolated yields (Eq. 24.30). However, the PNP ligands seem to have no impact in this type of catalysis as the respective metal chlorides also showed comparable reactivities.

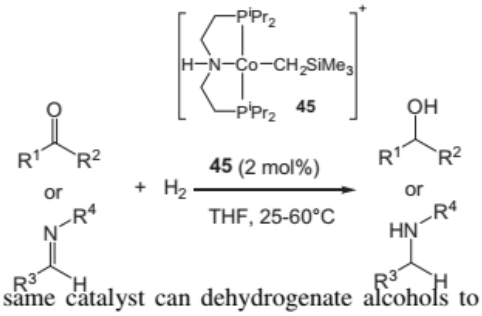


(24.30)

24.3 COBALT PINCERS

24.3.1 Ketone and Imine Hydrogenation/Dehydrogenation

In 2012, Hanson reported the preparation and hydrogenation chemistry of a cobalt PNP pincer complex, $[(^{i}Pr_2PCH_2CH_2NHCH_2CH_2P^{i}Pr_2)Co(CH_2SiMe_3)]^+$ [28], similar to the Ru-MACHO complex [29]. Formed by protonation with $HBAr^F$ of the neutral complex without a hydrogen on nitrogen, this cationic complex **45** was found to be active for the hydrogenation of activated ketones, such as acetophenone, and aliphatic ketones, such as 2-hexanone, at ambient temperature and 1 atm H_2 (Eq. 24.31). Aldehydes and imines were also quantitatively hydrogenated. Methylation of the cobalt-bound nitrogen gave a complex that was inactive toward these hydrogenations, implying a mechanism involving metal–ligand cooperativity.

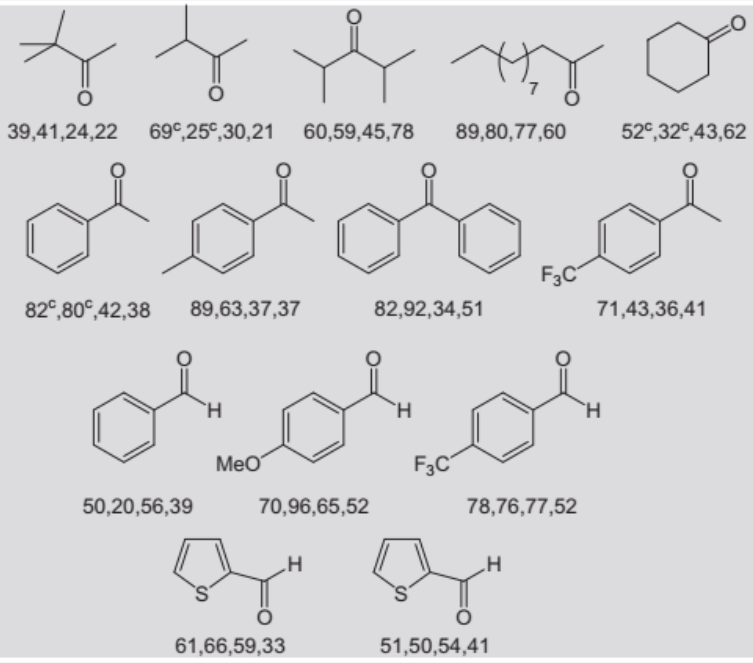


(24.31)

Hanson also discovered that this same catalyst can dehydrogenate alcohols to ketones [30]. Both 1-phenylethanol and cyclohexanol are converted to the corresponding ketone in quantitative yield. Curiously, dehydrogenation also occurs with the N-methyl derivative of the catalyst, suggesting a pathway that does not involve metal–ligand cooperativity.

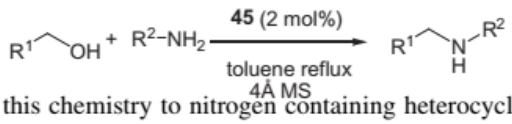
Combination of the alcohol dehydrogenation with a primary amine led to the formation of imine products in good yield [31]. Examination of the scope of reaction showed that benzylic, primary, and secondary alcohols all worked with

TABLE 24.1 Hydrosilation of Aldehydes and Ketones[a]



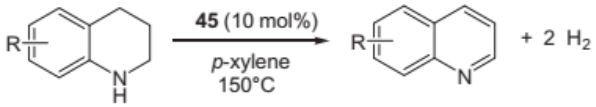
[a] [Cat] = ^{tBu}PNP-$FeCl_2$, ^{tBu}PNP-$CoCl_2$, ^{tBu}PONOP-$FeCl_2$, ^{tBu}PONOP-$CoCl_2$; [b]Conversion numbers calculated using GC–MS analysis; [c]After heating for 12 h.

benzylic, primary, and secondary amines. Zheng extended the scope of the reaction and also found that in the presence of 4 Å molecular sieves, the cobalt catalyst produced the reduced secondary amine product (Eq. 24.32) [32].



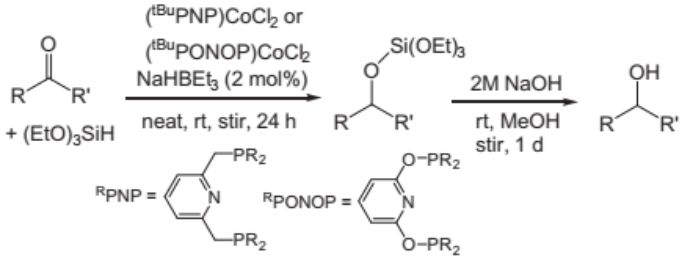
(24.32)

In 2015 Xu and Jones extended this chemistry to nitrogen containing heterocycles (Eq. 24.33). Here, tetrahydroquinoline is converted to quinoline by the same cobalt catalyst at 150°C. The use of a high temperature and a nitrogen-purged apparatus was required to drive the reaction to completion, as the dehydrogenation is uphill by 12.6 kcal/mol [33]. The presence of the heteroatom was found to be essential, as tetrahydronaphthalene and dihydronaphthalene were not dehydrogenated under the same conditions.



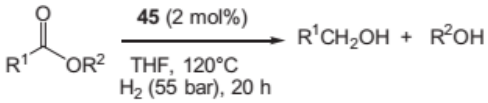
(24.33)

Findlater used PNP and PONOP cobalt(II) chloride pincer complexes for the hydrosilation of aldehydes and ketones (Eq. 24.34) and compared their reactivity to the corresponding iron(II) complexes (Table 24.1) [34]. He found that electron-withdrawing groups in the para-position of benzaldehyde showed increased reactivity, as demonstrated by competition experiments.



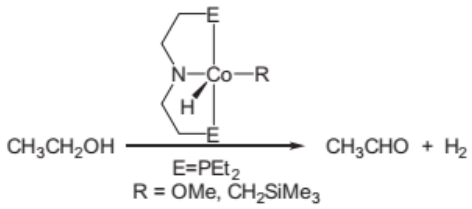
(24.34)

In 2017, Yuwen and Jones reported that the cobalt catalyst **45** discovered by Hanson above could also hydrogenate esters to alcohols [35]. The reaction proceeded in good yield at 120°C and 55 bar H_2 (Eq. 24.35). Both the N−H and N−Me derivatives of cobalt were effective catalyst precursors. Hydrogenation of lactones gave ring-opened diols. Methyl esters were found to make unsuitable substrates, however, as cleavage of the Me−O bond led to cobalt carboxylates that were ineffective as catalysts.

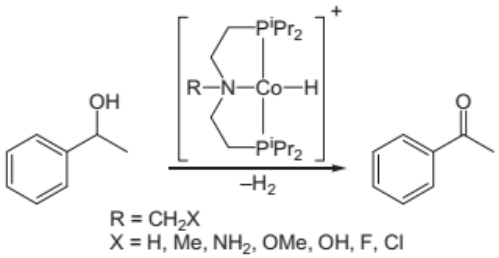


(24.35)

Yang has published the results of DFT calculations on the dehydrogenation of ethanol to acetaldehyde using a cobalt catalyst similar to **45** (Eq. 24.36). He found that ethanol assists in the proton transfer during the loss of H_2 from (PNHP)CoH_2, which lowers the barrier by almost 6 kcal/mol [36]. Calculations with the ^{iPr}PNP vs the ^{Et}PNP complex showed a barrier about 6 kcal/mol higher. He also calculated the barriers for dehydrogenation of 1-phenylethanol using $[(^{iPr}PNRP)CoH]^+$ catalysts where R = H or CH_2X, X = H, Me, NH_2, OMe, OH, F, Cl (Eq. 24.37). The parent N−H complex was found to have the lowest barrier, but formation of an alkoxide adduct reduces the activity of the catalyst.



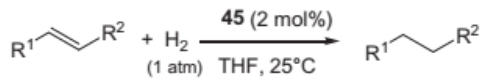
(24.36)



(24.37)

24.3.2 Alkene Hydrogenation

The cobalt PNP catalyst discovered by Hanson, **45**, was also found to be active for the hydrogenation of alkenes [28,30]. Both activated alkenes such as styrene, as well as simple alkenes such as 1-octene, are readily hydrogenated at 25°C and 1 atm H_2 (Eq. 24.38). Internal alkenes were hydrogenated, but trisubstituted alkenes were not hydrogenated. Remarkably, methylation of the ligand nitrogen group gives a complex that is still an active hydrogenation catalyst.

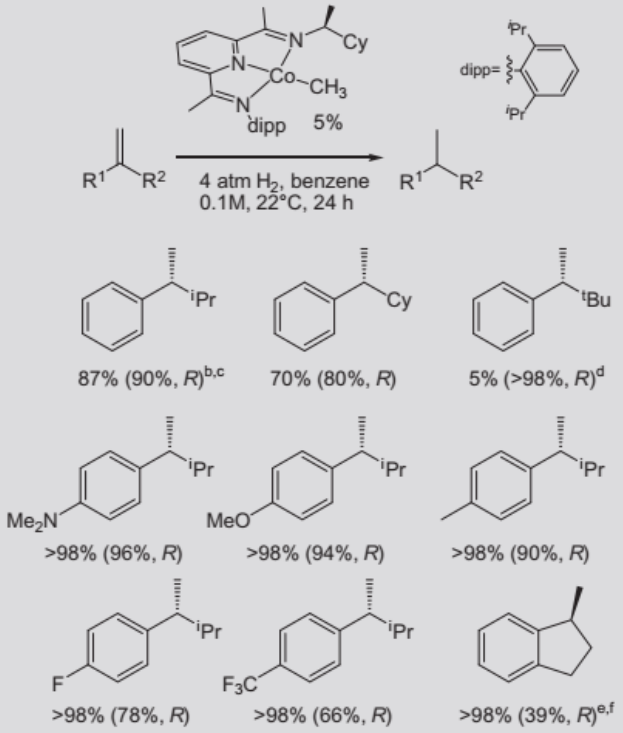


(24.38)

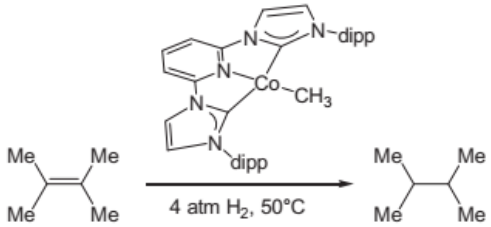
Following earlier studies by Budzelaar [37], Chirik reported that the PDI ligand on cobalt is effective for alkene hydrogenation also [38]. Use of a chiral group on the imine led to chiral hydrogenation products of geminal disubstituted alkenes in decent yield. Hydrogenation occurred at room temperature under 4 atm H_2 (Table 24.2). Lower e.e.'s were obtained with 1-methyleneindane, entry I, although use of a cyclohexyl catalyst precursor gave 96% e.e. 3-phenyl-1H-indenes were reduced to the chiral indanes with ~97% e.e. [39]. Use of D_2 showed evidence for syn addition of hydrogen. Chirik has also reviewed and compared iron and cobalt pyridinediimine catalysts for olefin hydrogenations [40].

Chirik also examined a pyridine-bis-NHC ligand to attach to cobalt(I) (Eq. 24.39). This complex is an effective catalyst for hydrogenation of sterically hindered, unactivated alkenes such as *trans*-methylstilbene [41]. Even 2,3-dimethyl-2-butene was hydrogenated. Evidence for noninnocent behavior of the ligand was seen when the hydride was exposed to N_2, as the hydride migrated to the 4-position of the pyridine as the N_2 coordinated to cobalt(I).

TABLE 24.2 Enantioselective Hydrogenation of Germinal Disubstituted Alkenes

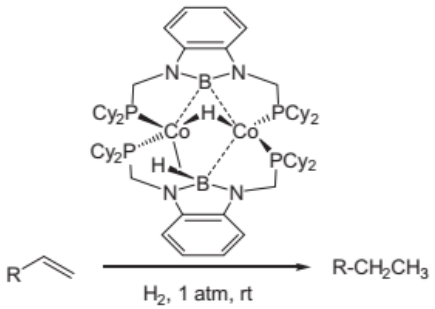


[a]Conditions: 0.1 mmol of olefin, 5 μmol of catalyst, 1 mL of benzene. Yields were determined by GC-FID; e.e.'s are shown in parentheses. [b]With (R)-2-Me: 85% (90% e.e.; S enantiomer). [c]With (^{iPr}PDI)Co(Me): 60%. [d]At 45 °C: 12% (0% e.e.). At 80 °C: 64% (0% e.e.). [e]Reaction time = 1 h. [f]With (S)-2-CM: 44% (96% e.e.; S enantiomer) and 56% 3-methyl-1H-indene.



(24.39)

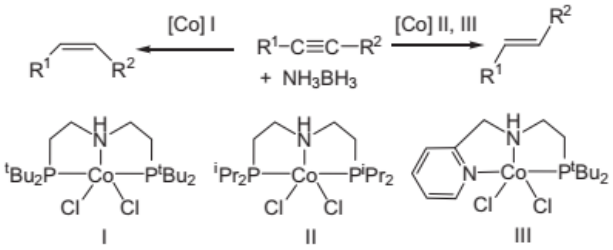
Peters reported a novel PBP pincer complex that hydrogenates a variety of olefins [42]. The hydride dimer first reacts directly with H_2, which is believed to react with olefin substrate to go on to product (Eq. 24.40).



(24.40)

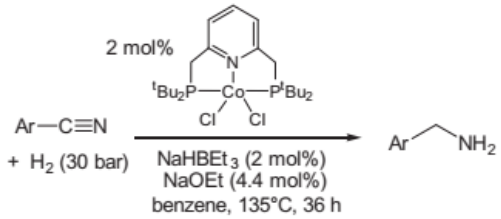
Liu has reported that (^{tBu}PNHP)$CoCl_2$ can hydrogenate diphenylacetylene using BH_3NH_3 as the hydrogen source [43]. A 94:5 ratio of *Z*:*E* stilbene is obtained (Eq. 24.41). With the less bulky ^{iPr}PNHP ligand on cobalt, a 8:92 ratio of

Z:E stilbene is obtained. Using an even less bulky pyridine-amine-phosphine pincer ligand gave entirely *E* product. Following the reaction profile over time showed a rapid hydrogenation to give *Z*-stilbene product, followed by a rapid $Z \rightarrow E$ isomerization. Hence, the *Z* selectivity seen with the ^{tBu}PNHP ligand can be ascribed to its poor ability to perform the $Z \rightarrow E$ conversion.



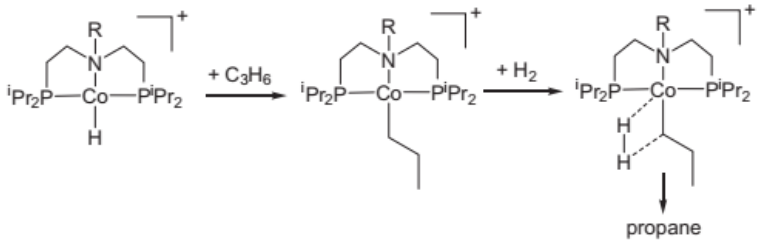
(24.41)

Milstein has reported that a cobalt-PNN complex can catalyze the hydrogenation of nitriles to primary amines [44]. A pressure of 30 bar H_2 and 135°C is required for hydrogenation to occur (Eq. 24.42). The reaction tolerated a variety of functional groups although aryl bromides gave poor yields.



(24.42)

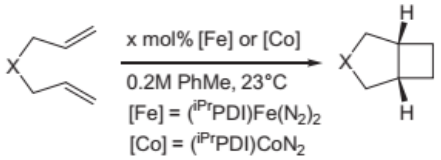
Yang has done DFT calculations on propene hydrogenation using a cobalt PNP pincer complex [36]. Using a cobalt hydride model complex (Eq. 24.43), he found that H_2 splitting was the rate limiting step, and that the N−H ligand had ~2 kcal/mol lower barrier than the N−Me ligand. The N−CH_2OH ligand derivative was predicted to be ~1 kcal/mol lower than the N−H ligand.



(24.43)

24.3.3 Alkene Polymerization and Cycloaddition

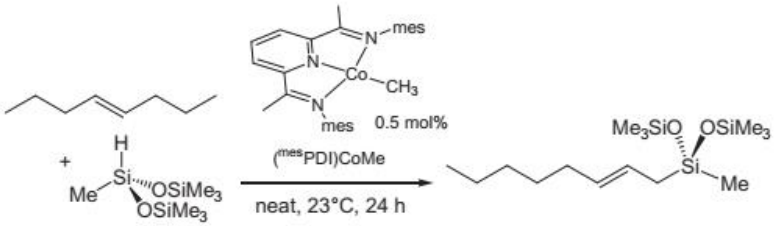
The cobalt pyridinediimine complex used by Chirik was also found to be capable of catalyzing a [2 + 2] addition of α,ω-dienes [45]. Here, the yield of product was highly dependent on the nature of the linking group joining the two olefins. The RN- linker proved to give far better yields (99%) than the O- linker (~65%), which is much better than the CH_2- linker (0%) (Eq. 24.44). An η^2,η^2-diene complex was identified as an intermediate. Chirik has reviewed the use of cobalt and iron PDI complexes for alkene polymerization and cycloaddition [46].



(24.44)

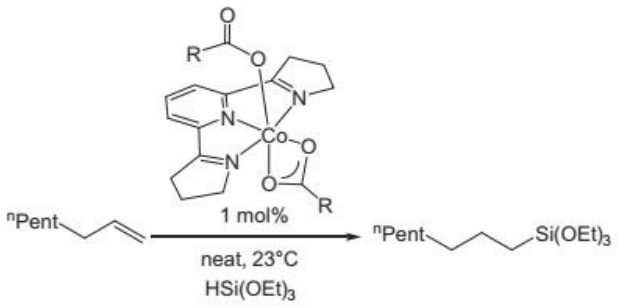
24.3.4 Alkene Hydrosilation

The cobalt pyridinediimine catalysts have also found applications in olefin hydrosilation [47]. Reaction of an internal olefin with a tertiary silane produced allylic silane products in 98% yield using only 0.5% catalyst at room temperature (Eq. 24.45). Some primary and secondary silanes gave complete reaction in only 15 min, whereas Et_3SiH required about an hour to go to completion. Furthermore, the silane is located only at the terminus of the alkyl chain. Stoichiometric experiments and deuterium labeling studies support activation of the cobalt alkyl precursor to form a putative cobalt silyl, which undergoes 2,1-insertion of the alkene followed by selective β-hydrogen elimination from the carbon distal from the large tertiary silyl group and accounts for the observed selectivity for allylsilane formation.



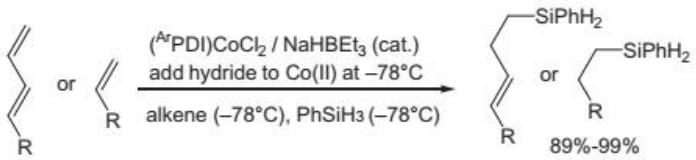
(24.45)

Chirik has also prepared a bis-dihydropyrrole-pyridine complex for alkene hydrosilation [48]. Here the product is the saturated alkylsilane, with catalyst TONs approaching 4000. The catalyst itself is air-stable and can be handled on the benchtop. They also found that use of ethylhexanoate instead of acetate ligands on the cobalt catalyst precursor led to higher reactivity (Eq. 24.46).



(24.46)

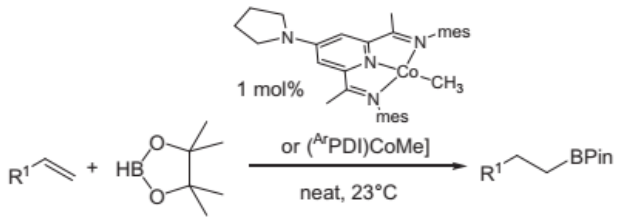
In related work, Rajanbabu used a cobalt(II) PDI precursor in the presence of borohydride to generate a catalyst for 1,3-diene hydrosilation [49]. The products are those arising from antiMarkovnikov 1,2-hydrosilation without disturbing the internal double bond (Eq. 24.47). The reaction is tolerant of various functional groups. Simple alkenes give 1,2-addition products.



(24.47)

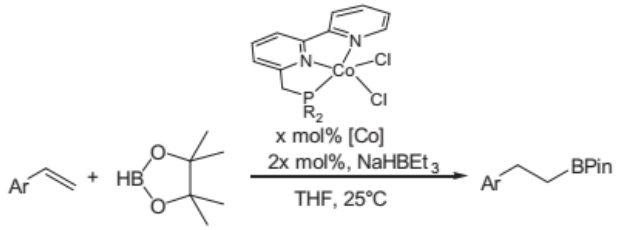
24.3.5 Alkene Hydroboration

The PDI-cobalt catalyst discussed above is also active for alkene hydroboration (Eq. 24.48). Reaction of neat 1-octene with HBPin in the presence of 1% catalyst at room temperature produced terminal borolated product in 15 min in 98% yield [50]. Internal olefins also give terminal borane products, indicating that double bond isomerization is rapid. The fastest catalyst was one in which the 4-position of the central pyridine is substituted by a pyrrolidine group. Even tetra-substituted olefins such as 2,3-dimethyl-2-butene react in high yield.



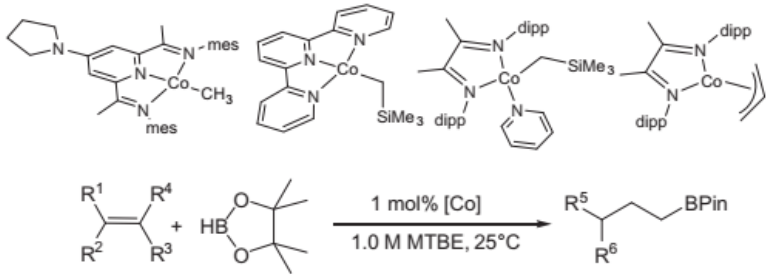
(24.48)

Huang reported the use of a PNN pincer on cobalt (II) for olefin hydroboration, where PNN refers to a bipy ligand with a pendant $-CH_2P^iPr_2$ group. Borohydride was used to activate the catalyst. As little as 0.05% catalyst could be used to give 97% yield of product upon coupling styrene with HBPin (Eq. 24.49). Many other terminal olefins reacted to give high yields of antiMarkovnikov product (80%−97%).



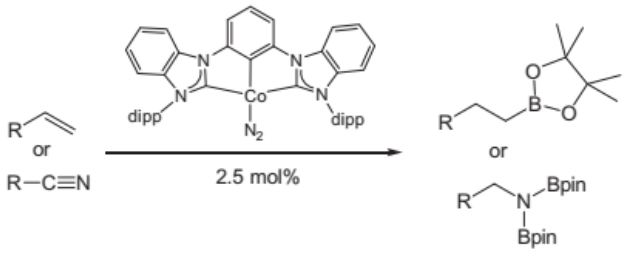
(24.49)

Chirik compared four cobalt catalysts for alkene hydroboration [51]. These include the PDI-Co catalyst described in Eq. 24.48, a simple terpy-cobalt alkyl derivative, an α-diimine cobalt alkyl complex, and an allyl cobalt α-diimine complex (Eq. 24.50). While all catalysts worked well for hydroboration of terminal olefins, reaction with "difficult" olefins such as t-butylethylene or 1,1-dicyclohexylethene showed that the α-diimine complexes were superior catalysts. This reactivity was ascribed to the lower electron count of the α-diimine substituted cobalt catalysts, allowing reductions of tri-, tetra-, and gem-disubstituted olefins. The terpy catalyst was found to be effective with substrates containing dienes or arene groups.



(24.50)

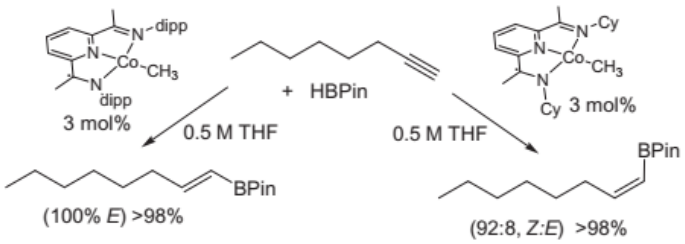
Fout has recently reported a bis-NHC aryl pincer complex of Co(I) that catalyzes alkene hydroboration [52]. Reaction with HBPin occurs at ambient temperature to give the antiMarkovnikov addition product (Eq. 24.51). This CCC pincer complex also allows nitriles to be doubly hydroborated at 70°C. The hydroboration of 4-vinylcyclohexene, a substrate bearing both an internal alkene and a terminal alkene, proceeded selectively at the terminal alkene position, with complete retention of the internal olefin. More sterically hindered substrates (e.g., gem-disubstituted alkenes) did not undergo hydroboration.



(24.51)

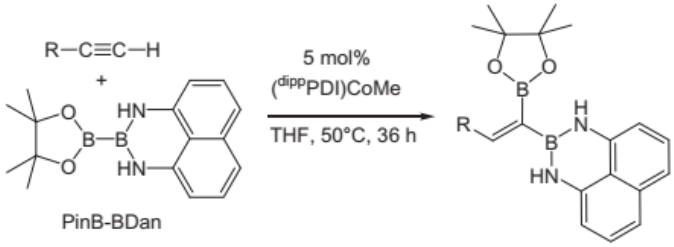
24.3.6 Alkyne Hydroboration

Just as alkenes are readily hydroborated by cobalt pincer catalysts, alkynes undergo a single addition of pinacolborane in the presence of (^{Cy}PDI)CoMe [53]. A 92:8 ratio of *Z*:*E* isomers is obtained in high yield (Eq. 24.52). Use of the DIPP derivative of the PDI ligand, however, gives the *E*-isomer exclusively. The difference in selectivity was attributed to the differing relative rates of addition of the acetylene C−H bond versus the pinacolborane B−H bond for the two catalysts. Alkyne C−H addition leads to the *Z*-product, whereas reaction with B−H leads to the formation of a cobalt hydride that produces the *E*-product.



(24.52)

Chirik also examined the reactivity of terminal alkynes with B_2Pin_2 [54]. Reaction occurs at ambient temperature to give the gem-diborylated alkene. Use of an asymmetric diborane showed that both borons are transferred to the same alkyne—there is no crossover (Eq. 24.53).



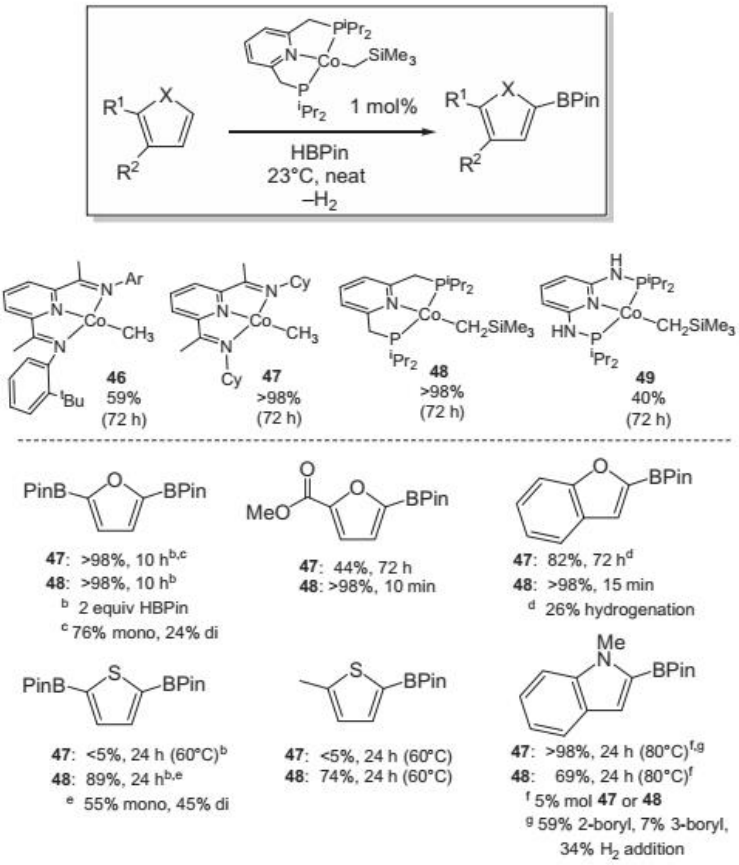
(24.53)

24.3.7 Arene Hydroboration

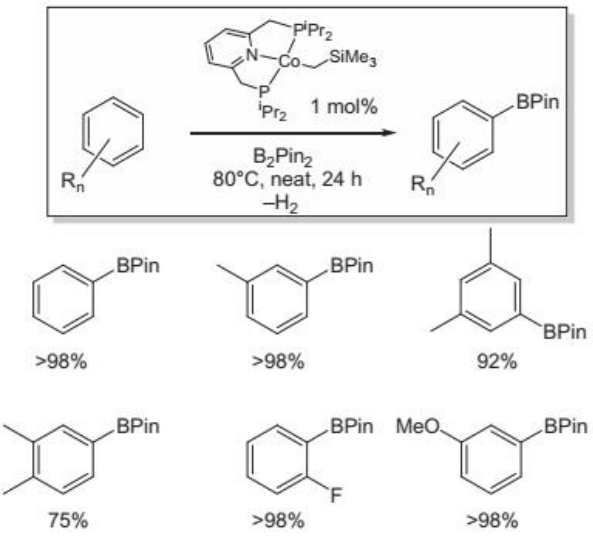
Several cobalt PNP and NNN pincer catalysts were examined by Chirik for the borylation of thiophenes and furans using HBPin [55]. As shown in Scheme 24.1, the ^{iPr}PNP complex **48** generally gives the highest yields, although the ^{Cy}PDI complex **47** is occasionally superior. Pyridine derivatives were also borylated using B_2Pin_2 in good yield using the ^{iPr}PNP catalyst at 80 °C, with HBPin appearing as a side product. Arenes are also borylated under these conditions giving monoborylated derivatives in good yield (Scheme 24.2). Reaction is proposed to occur via (^{iPr}PNP)CoH and (^{iPr}PNP)Co(BPin) intermediates. The borylation of 2,6-dimethylpyridine using complex **48** was investigated in detail by isolation of catalytic intermediates, performing stoichiometric experiments, and making kinetic measurements on the reaction. These studies revealed that the catalytic cycle operates via a Co(I) − Co(III) redox couple where the C − H activating species is a cobalt(I) boryl intermediate and the turnover limiting step is C − H oxidative addition of the arene [56]. In addition, catalyst deactivation was found to occur by borylation of the 4-position of the arene ring in **48**. Introduction of a pyrrolidine functionality in this position not only prevented catalyst deactivation, but also improved reactivity due to the enhanced electron-donating ability of this pincer ligand.

A separate report compared eight different cobalt(II) dichloride pincer complexes (Fig. 24.1) for borylation of sp^2 C−H bonds using either HBPin or B_2Pin_2 [57]. Furans, pyridines, and arenes were all investigated and compared, with $HBEt_3^-$ being used to activate the catalysts. Complex **45-Cl$_2$** showed the greatest reactivity overall, with B_2Pin_2 giving the highest yields. The electron-donating ability of the pincer was cited as giving rise to the high activity.

Chirik also examined borylation of fluoroarene substrates using B_2Pin_2 and a cobalt PNP complex [58]. A strong preference for borylation adjacent to fluorine in the least hindered position was observed (Eqs. 24.54, 24.55). This selectivity is the opposite of what is seen with iridium-based borylation catalysts [59,60], and no secondary borylation was observed.



SCHEME 24.1 C-H functionalization with (PNP)$CoCH_2SiMe_3$.



SCHEME 24.2 Arene functionalization with (PNP)$CoCH_2SiMe_3$.

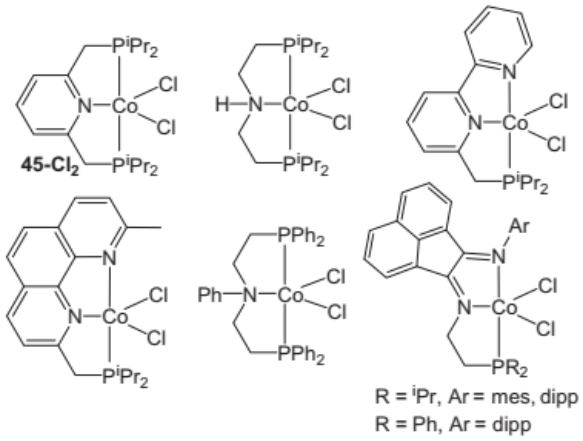
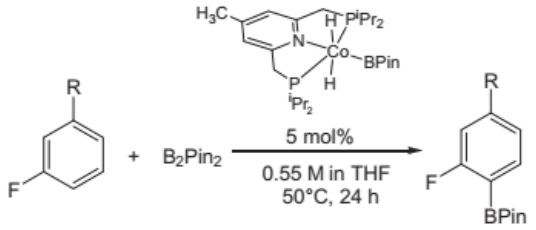
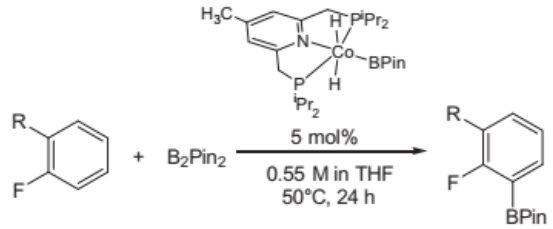


FIGURE 24.1 Cobalt pincer complexes for arene borylation.

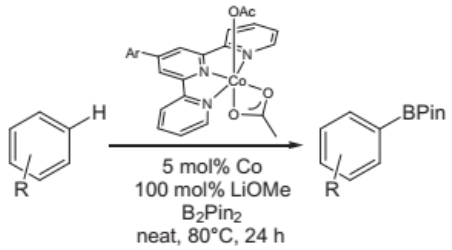


(24.54)



(24.55)

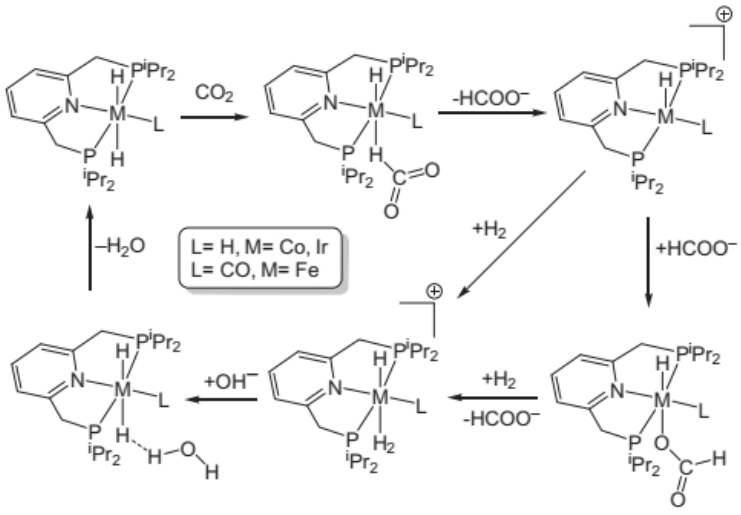
Most recently, Chirik has reported a terpyridine cobalt catalyst for arene borylation [61]. The complex is air stable, and TONs of up to 100 were obtained (Eq. 24.56). The highest activity was seen with the ligand in which Ar = 4-dimethylaminephenyl. Catalyst deactivation ultimately occurs from reaction with HBPin to give $Co[PinB(OAc)_2]_2$ and $(ArTpy)_2Co$.



(24.56)

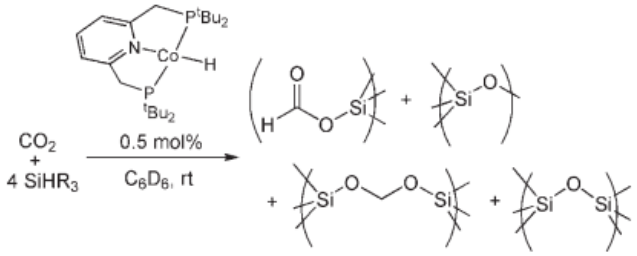
24.3.8 Reactions With CO_2

In 2009, Nozaki reported an iridium pincer catalyst, (^{iPr}PNP)IrH_3, that displays an unprecedented reactivity for CO_2 reduction by H_2 to produce HCOOK with TONs of 3,500,000 and TOFs of 150,000 h^{-1} [62]. Ahlquist performed DFT calculations on this system [63], and Yang examined the cobalt and iron analogs for comparison [64]. The pathway follows a hydride transfer (from M−H to CO_2)/proton transfer (from M−H_2 to OH^-) sequence (Scheme 24.3). While hydride transfer was rapid for all of these systems, proton transfer was found to have the largest barrier, varying from 18.6 to 21.9 to 22.6 for the Ir, Fe, and Co complexes.



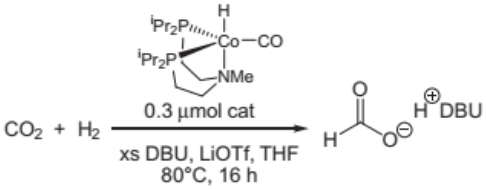
SCHEME 24.3 Proposed pathway for CO_2 reduction using (PNP)$CoCH_2SiMe_3$.

Chirik examined the reduction of CO_2 using the complex (^{tBu}PNP)CoH as catalyst (PNP = bis(phosphino)pyridine) and a primary silane as hydrogen source [65]. With 0.5 mol% catalyst, CO_2 and $PhSiH_3$ react to give a mixture of silyl formates, bis(silyl)acetyls, and silyl ethers (Eq. 24.57). The distribution of products changes over time, with the first-formed silyl formates going on to produce bis(silyl)acetyls and silyl ethers. Stoichiometric reaction gives $PhH_2SiOCH_2OSiPhH_2$ and (^{tBu}PNP)$CoH_2(SiH_2Ph)$ cleanly.



(24.57)

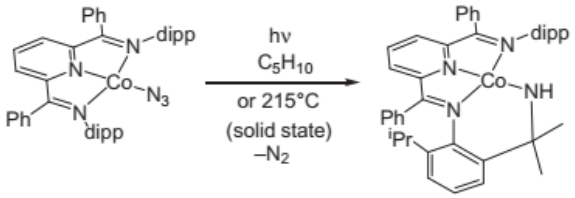
Bernskoetter has examined the N-Me derivative (^{iPr}PNMeP)Co(CO)H for CO_2 reduction (^{iPr}PNMeP = $^{i}Pr_2PCH_2CH_2NMeCH_2CH_2P^{i}Pr_2$) [66]. Reaction at 80°C in the presence of excess DBU and LiOTf base gives formate$^-$ $(HDBU)^+$ in about 12% conversion and 9400 turnovers (Eq. 24.58). Other catalyst precursors showed similar reactivity.



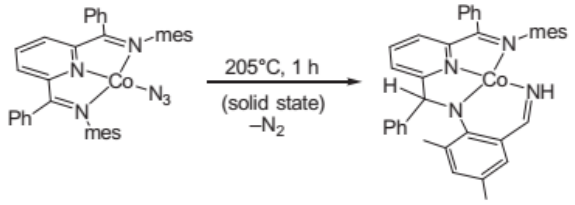
(24.58)

24.3.9 Miscellaneous Reactions of Cobalt Pincer Complexes

Chirik described synthetic routes that led to pyridinediimine complexes with azide ligands [67]. Irradiation in pentane led to ejection of N_2, and the nitride complex inserts into the adjacent C−H bond of an isopropyl group (Eq. 24.59). In the mesityl-substituted PDI complex, insertion into a methyl C−H is followed by migration of a hydrogen atom from the CH_2 group to one of the PDI imine carbon atoms, resulting in an interchange of the amido and imine functionalities (Eq. 24.60).

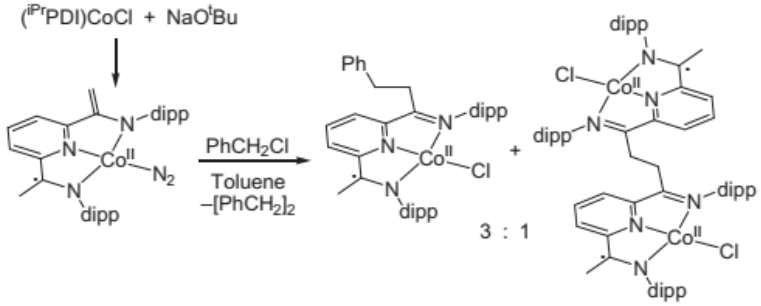


(24.59)



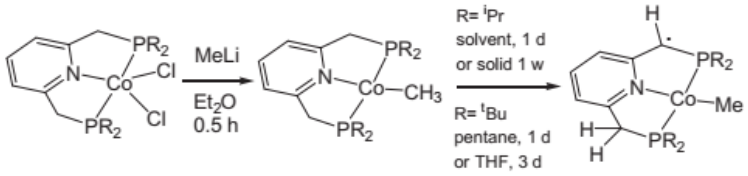
(24.60)

Deprotonation of a pyridinediimine cobalt(II) chloride complex gives a product in which one imine is converted to an amido ligand (Eq. 24.61). Reaction of this species with benzyl chloride results in two products arising from Cl atom abstraction and trapping of the benzyl radical that is formed [68]. The reactivity is attributed to the antiferromagnetically coupled diradical nature of the (^{iPr}PIEA)CoN_2 intermediate.



(24.61)

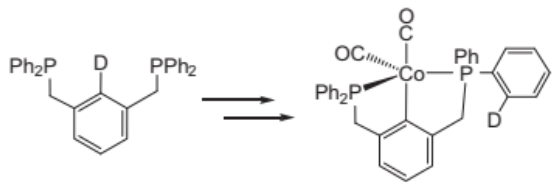
Milstein found that the bis(phosphino)pyridinecobalt methyl complex shown in Eq. 24.62 undergoes spontaneous formal loss of a hydrogen atom from one of the "arms" [69]. The fate of the H atom was not determined, but in the presence of diphenylacetylene, stilbene is observed. Milstein indicates that homolysis of a C−H bond is unlikely, and that some agent must be present to accept the H atom.



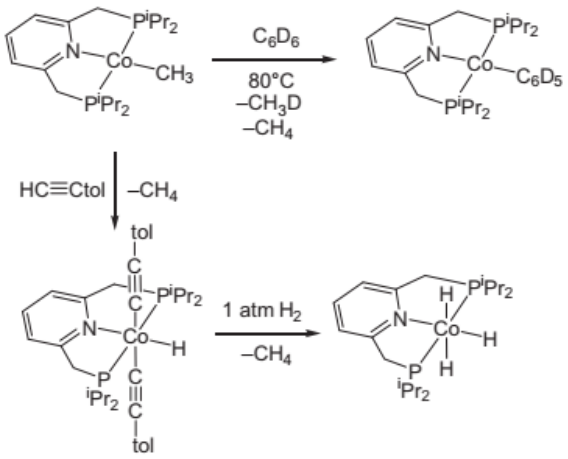
(24.62)

Chirik has found that the diamagnetic bis(phosphino)pyridinecobalt methyl complex reacts with H_2 to give methane and the (^{iPr}PNP)CoH_3 complex [70]. Reaction with tolylacetylene leads to double C−H oxidative addition to produce (^{iPr}PNP)CoH(C≡Ctol)$_2$. Reaction with C_6D_6 yields the perdeuterophenyl product (^{iPr}PNP)Co(C_6D_5) (Scheme 24.4).

In examining the formation of a cobalt PCP pincer complex, Pringle reacted the monodeuterated PNP pincer ligand with $MeCo(PMe_3)_4$ and CO [71]. The expected product was obtained, but he found that the ortho position of the phenyl groups on the pincer were ~15% deuterated (Eq. 24.63). This observation indicated that during the cyclometallation to make the PCP pincer, the hydride can be transferred to an orthometallated phenyl group.

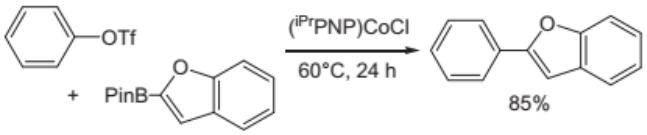


(24.63)



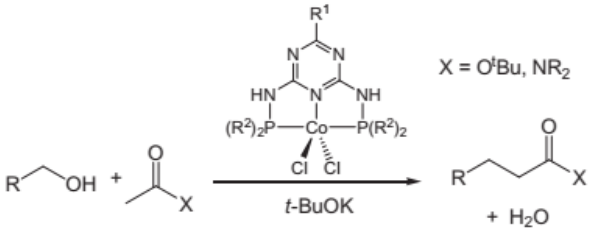
SCHEME 24.4 C-H activations by (PNP)$CoCH_3$.

In his studies of sp^2 C−H borylation, Chirik found that a PNP cobalt pincer complex can act as a catalyst for a Suzuki-Miyaura coupling reaction [72]. Heating a 1:1:1 mixture of PhOTf, 2-benzofuranyl-BPin, and NaOCH(Ph)Me in the presence of 5 mol % (^{iPr}PNP)CoCl in THF at 60 °C for 24 h resulted in formation of 2-phenylbenzofuran in 85% yield (Eq. 24.64). Pyridyl triflate and fluorophenyl triflate gave low yields. While a number of substituted furanyl boronates gave good yields, benzothiophenyl and indolyl boronates gave no product.



(24.64)

Kempe has examined a PNP cobalt pincer with a highly nitrogen substituted ligand [73]. He found that this complex is a catalyst for the alkylation of esters and amides (Eq. 24.65).

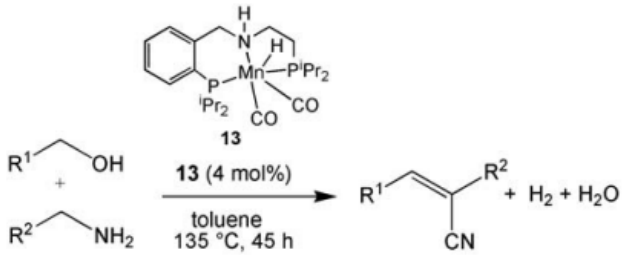


(24.65)

24.4 RECENT ADDITIONS

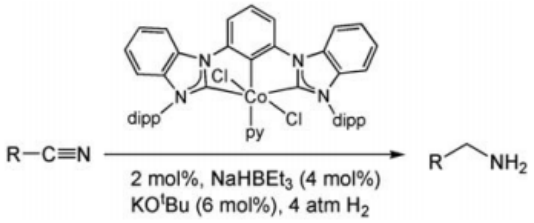
During the preparation of this chapter and prior to publication a few relevant recent reports have appeared on manganese and cobalt pincer complexes. Several of the references that have appeared are appended here for completeness.

Milstein has reported that manganese complex **13** with an asymmetric PNP pincer ligand that is effective for the acceptorless dehydrogenative coupling of primary alcohols and primary amines to give α,β-unsaturated nitriles (Eq. 24.66). This catalyst proved to be far superior to complex **5** in Eq. (24.3), showing broad scope and providing good yields [74].



(24.66)

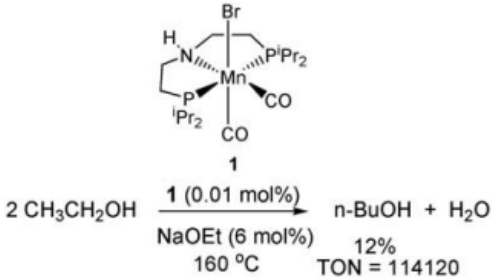
Fout has reported that nitriles can be reduced to primary amines using a cobalt(III) variant of the Co−bis−NHC aryl pincer complex shown earlier (Eq. 24.67). Here, triethylborohydride serves to generate the catalyst in situ, and 4 atm H_2 are employed in the reduction [75]. Her group also reported that the cobalt complex (MesCCC)Co(H_2)(PPh_3) (MesCCC = bis(mesityl-benzimidazol-2-ylidene)phenyl) was active for the hydrogenation of terminal olefins [76] and the *E*-selective partial hydrogenation of internal alkynes to alkenes [77].



(24.67)

Bernskoetter prepared the $[(^{iPr}PNHP)Co(CO)_2]^+$ variant of the $[(^{iPr}PNMeP)Co(CO)_2]^+$ complex shown in Eq. (24.58) and examined its reactivity for CO_2 reduction with H_2. Surprisingly, he observed a 50-fold decrease in formate turnover (TON = 450 vs. 29,000) under identical conditions [78]. This led him to conclude that metal−ligand cooperativity is not involved in the CO_2 reduction reaction. The ^{Cy}PNMeP ligand was also examined, and found to have lower reactivity than the *i*-propyl derivative.

Liu has reported that the manganese ^{iPr}PNHP pincer complex **1** can be used in the Guerbet reaction to convert upgrade ethanol to butanol as shown in Eq. (24.68) [79]. They report very high turnover numbers (over 100,000) and selectivities (92%) at low conversions (<12%) using low catalyst concentrations (0.01%). Kulkarni and Jones also reported on the activity of this system but at higher catalyst loadings (0.5%−5%). Higher conversions were observed (up to 86%) at the expense of selectivity for 1-butanol [80]. The optimized system showed a 22% yield of 1-butanol at 37% conversion of ethanol. Only 3% of the higher Guerbet alcohols (C_6−C_{10}) were formed, with the remainder of the ethanol being dehydrogenated to make sodium acetate and H_2 gas.



(24.68)

Some common abbreviations used in this chapter include:

TON = turnover number
TOF = turnover frequency
PDI = pyridine-2,6-diimine
PCP = a pincer with outer P donors, a central C donor, and CH_2 linkers
PNP = a pincer with outer P donors, a central N donor, and CH_2 linkers
POCOP = a pincer with outer P donors, a central C donor, and O linkers
PONOP = a pincer with outer P donors, a central N donor, and O linkers
$HBAr^F$ = H^+ $[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-$, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

NHC = N-heterocycliccarbene
DIPP = 2,6-diisopropylphenyl
HBPin = HBpinicolate
TPY = terpyridine

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