Pincer Transition Metal Catalysts for Sustainability

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Sustainable solutions are needed to avoid global warming and climate change. Homogeneous catalysis might play a fundamental role for this. Pincer-type complexes are promising in terms of stability, selectivity, efficiency and the use of mild reaction conditions. Pincer complexes have been used in many sustainable chemical reactions, for example hydrogen release and upconversion of CO2, N2, and biomass.

pincer complexes
sustainability
biomass valorization
hydrogen
carbon dioxide valorization
nitrogen fixation

1. Introduction

Pincer complexes are highly promising catalysts for numerous sustainable processes. High catalytic activity under mild reaction conditions, low catalyst loading, and high selectivity are the general main advantages important for sustainable reactions as guided by the green chemistry guidelines [1]. Increased robustness because of the pincer stabilization results in increasinly stable homogeneous catalytic systems [2][3][4].

The pincer complex, of the PCP type, was synthetized by Shaw in 1976 [5]. Numeous pincer complexes have since been synthetized as well as used in catalysis [6][7][8][9][10][11][12][13][14][15][16][17][18][19][20][21][22][23][24][25][26][27][28][29][30][31][32][33][34][35][36][37][38][39][40][41][42][43][44][45][46][47][48][49][50][51][52][53][54][55][56][57][58][59][60][61][62][63][64][65][66][67][68][69][70][71][72][73][74][75][76][77][78][79][80][81][82][83][84][85][86][87][88][89][90][91][92][93][94][95][96][97][98][99][100][101][102][103][104][105][106][107][108][109][110][111][112][113][114][115][116][117][118][119][120][121][122][123][124][125][126][127]. Examples are [128][129][130], hydroamination [131][132][133], hydrocarboxylation [134], hydrovinylation [135], aminomethylation [136], alkane dehydrogenation [137][138][139][140][141][142], alkane metathetis [143], amine N-formylation [144][145], secondary alcohol C-alkylation [146][147], ketone α-alkylation [148][149], and amine alkylation [150][151][152][153][154], aniline alkylation [155], vicinal diol deoxydehydration [104][105][156][157][158][159], and water splitting [12][160][161][162][163][164][165][166][167].

2. Dehydrogenation Reactions

2.1. Early Works

In the 1960s, Charman showed the first example of acceptorless alcohol dehydrogenation by homogeneous catalysis [168]. In the mid-1970s, Robinson demonstrated the dehydrogenation of isopropanol, 1-butanol, ethanol, methanol, and glycerol [169][170][171][172]. In 2004, Milstein presented the first example of metal–ligand cooperating pincer ligands in AAD for synthetic purposes [173][174]. In 2015, Li reported computational mechanistic studies on several reactions using the Milstein PNP and PNN catalysts [175]. Simultaneously, the Beller group started exploring the in situ influence of various phosphines and nitrogen containing ligands mixed with ruthenium catalyst precursors for the dehydrogenation of isopropanol [176]. In a following work from 2011, Beller tested both known catalyst as well as the in situ formation of active species using combinations of Ru-precursors and *N*-containing pincer ligands. In 2013, Beller showed the efficient conversion of ethanol into ethyl acetate using **Ru-MACHO**, reported in 2012 to efficiently catalyze ester hydrogenation [177]. In 2014, Beller showed that it is feasible to generate hydrogen from ethanol/water mixtures as well as from industrial bio-ethanol obtained from fermentation processes, without prior removal of the water content (5%) [178].

2.2.1. Methanol Dehydrogenation

In 2017, Beller proposed a manganese catalyst for aqueous methanol dehydrogenation [179]. Ethanol, paraformaldehyde, and formic acid were also dehydrogenated. Beller also showed that an iridium-PNP catalyst promotes methanol dehydrogenation under mild conditions [180]. In 2019, Beller improved the activity of Ru-PNP catalysts for methanol dehydrogenation using a bi-catalytic system [181].

2.2.2. Formic Acid Dehydrogenation

Formic acid as hydrogen carrier and storage system has been reviewed in many works [182][183][184][185][186][187][188][189][190][191][192][193]. For example, Milstein showed iron pincer complexes with a lutidine moiety as catalysts for hydrogenation of ketones [194][195], CO_2 hydrogenation to formate [196], and formic acid dehydrogenation [197].

3. Hydrogenation Reactions

Pincer complexes have been used in the (transfer) hydrogenation of many substrates, such as ketones [194][198][199][200][201][202][203], esters [38][204][177][195][205][206][207][208][209][210][211][212][213][214][215][216][217][218][219][220], aldehydes [221][222][223], amides [65][224][225][226][227][228], and imines [229][230].

CO_2 is potentially a C1 building block, increasing sustainability [231][232][233]. CO2 capture from the atmosphere or from localized emission sources have been studied [234][235][236][237][238][239][240][241][242][243]. CO_2 is subsequently stored ior utilized in synthesis of value-added products [244][245][246][247][248][249]. The industry uses several million tons of CO_2 for producing e.g. urea, salicylic acid, cyclic carbonates, and polypropylenecarbonate [250][251][252].

Catalytic hydrogenation of CO_2 has gained attention for storing green hydrogen with seminal works by Asinger [253], Leitner [254][255], Noyori [256], and Olah [257][258][259][260]. The synthesis of methanol from CO_2 is typically carried out at high temperatures and pressures by heterogeneous catalysts such as $Cu/ZnO/Al_2O_3$ [261][262][263][264]. Homogeneous catalytic systems have been usedfor the hydrogenation of CO_2 into green fuels [265][266][256][267][268][269][270][271][272][273][274][275][276][277][278][279][280][281][282][283][284][285][286].

3.1. CO_2 Hydrogenation

3.1.1. Early Works

The hydrogenation of carbon dioxide by means of homogeneous catalysis has grown extensively in the last decade. An overview of the best performing systems for CO_2 hydrogenation up to 2010 can be found in the work of Beller [287], while in 2018 and 2019 Prakash reviewed the topic in depth including the use of pincer type complexes [288][289].

Up to 2010, the best performing catalytic system was represented by the iridium-PNP catalyst **9**, reported by Nozaki in 2009, which overcame previously reported Ru [290][291][292][293], Rh [294][295][296], and Ir [297] homogeneous systems. In 2011, Milstein and co-workers published the first example of hydrogenation of carbonates into alcohols and carbamates into alcohol and amines as an indirect route for the synthesis of methanol from CO_2 [298]. The same year, Sanford proposed a cascade reaction mechanism for CO_2 hydrogenation using the Milstein catalyst **24-H** in combination with other two homogeneous catalysts, i.e., $(PMe_3)_4Ru\text{-}(Cl)(OAc)$ and $Sc(OTf)_3$ [299]. In 2011, Leitner performed computational studies on 38 different rhodium pincer alkyl complexes with varied steric and electronic environment for the CO_2 association and insertion into the metal–carbon bond, resulting in the corresponding carboxylate species [300]. In 2015, Leitner employed catalyst **55** for the hydrogenation of CO_2 into methanol without the need of an alcohol additive [301].

3.1.2. CO_2 Hydrogenation to Methanol

In 2016, Himeda and Laurenczy reported an iridium complex to catalyse bicarbonate hydrogenation to formate as well as formic acid dehydrogenation [302], and for the production of methanol from CO_2 in the presence of sulfuric acid [303]. In 2015, Sanford employed a ruthenium-based catalytic hydrogenation of CO_2 to methanol with dimethylamine as capturing agent [304]. The same year, Milstein developed indirect CO_2 hydrogenation by prior CO2 capture by amino alcohols followed by hydrogenation of the resulting oxazolidinone to form MeOH [305]. The year after, Olah and Prakash demonstrated a catalytic system for a one-pot CO_2 capture as well as conversion to methanol employing polyamine and Ru-MACHO-BH [306]. In 2018, Prakash showed another system for the integrative CO_2 capture (trapped in the form of carbamate and bicarbonate salts) followed by hydrogenation to methanol, using a biphasic 2-methyltetrahydrofuran (2-MTHF)/water solvent system [307].

3.1.3. CO_2 Hydrogenation to Formate Salts

In 2014, Hazari and Schneider demonstrated Fe-PNP complexes as catalysts with a Lewis acid as co-catalyst for the dehydrogenation of formic acid [308]. One year later, the hydrogenation of CO_2 catalyzed by the same system was demonstrated by Hazari and Bernskoetter [309]. In 2016, a comprehensive overview of the state-of-the-art for CO_2 hydrogenation, as well as formic acid/methanol dehydrogenation using first-row metal complexes, was published by Bernskoetter and Hazari [310]. The authors provide comparisons between selected iron and cobalt pincers with known Ru-PNP catalysts, and investigate the role of Lewis acid additives in the improvement of these promising base metal catalysts. The same year, Bernskoetter showed the synthesis, as well as crystallographic characterization, of cobalt(I)-PNP complexes derived from the pincer ligand $Me\text{-}N[CH_2CH_2(P^iPr_2]_2$ [311].

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