Polyhedron 180 (2020) 114416

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Bisoxazoline-pincer ligated cobalt-catalyzed hydrogenation of alkenes

Mikhaila D. Ritz [1], Astrid M. Parsons [1], Philip N. Palermo, William D. Jones *

Department of Chemistry, University of Rochester, 404 Hutchinson Hall, Rochester, NY 14627-0216, United States

ARTICLE INFO

Article history:
Received 11 December 2019
Accepted 27 January 2020
Available online xxxx

Keywords:
Cobalt
Pincer
Hydrogenation
Oxazoline
Alkenes

ABSTRACT

The efficient and atom economical hydrogenation of alkenes using a novel bisoxazoline ligated cobalt complex has been developed. The hydrogenation of a variety of alkenes containing electron neutral and electron-donating groups proceeds in high yield, while electron-withdrawing and sterically hindered groups are not tolerated. Heterocycles and internal alkenes were also hydrogenated in moderate to high yields. While the catalyst is enantiopure, no enantioinduction was observed suggesting that other factors are involved in achieving enantiocontrol.

1. Introduction

Earth-abundant metal complexes can catalyze a range of organic transformations, including (de)hydrogenation, borylation, hydrosilylation, and C—C bond formation [1–3]. In particular, catalytic hydrogenation reactions using molecular hydrogen as the reducing agent has attracted the attention of many scientists as this atom-economic transformation provides access to intermediates and bulk products [4,5]. While many catalytic systems for the hydrogenation of alkenes exist, most rely on noble metals such as iridium [6–8], rhodium [9–11], ruthenium [12–14], and palladium [15,16]. Recently, the use of 3*d* transition metal complexes has been explored due to their abundancy, non-toxicity, and cost [17]. However, working with first-row transition metal complexes comes with its own set of challenges as these can often undergo one electron pathways, less prevalent with their second and third row counterparts and thus making their reactivity difficult to predict and/or control [18]. Despite these challenges there have been many recent advances in this field specifically involving cobalt [1,3,19].

In 2012, Hanson and co-workers reported the hydrogenation of C = X (X = C, O, N) bonds utilizing a square-planar 15-electron cobalt (II)-alkyl complex (see Scheme 1) [20]. This system was able to hydrogenate a variety of ketones, imines, and alkenes under 1–4 atm of H_2 over the course of 24–65 h. Furthermore, Zhang et al. reported the use of this same complex for the transfer hydrogenation of olefins [21]. A range of aliphatic, aromatic, internal, and cyclic alkenes were hydrogenated, however, this transformation is not atom economical due to the excess amount of hydrogen donor needed. Furthermore, in 2016, Fout reported a monoanionic bis(carbene) ligated cobalt complex that allowed for the hydrogenation of simple alkenes [22].

Success has also been shown using asymmetric ligands on cobalt to enact hydrogenation reactions. Following the seminal work shown by Ohgo [23] and Pfaltz [24], in 2016, Chirik reported on the hydrogenation of cyclic alkenes catalyzed by a C_1-symmetric bis(imino)pyridine cobalt catalyst [25]. The hydrogenation of minimally functionalized benzofused five,- six,- and seven-membered alkenes was explored giving rise to important substructures of natural and biologically active products. Similarly, Lu et al. reported an oxazoline-iminopyridine cobalt complex that catalyzed the hydrogenation of a variety of 1,1-diarylethenes [26]. While this transformation was enantioselective, chlorine groups in the ortho position were necessary to achieve high enantioselectivity. Additionally, Liu and Huang reported on the enantioselective hydrogenation of vinyl silanes utilizing a C_1 asymmetric phosphine-pyridine oxazoline ligated cobalt complex [27]. While a wide range of functionalized vinylsilanes were tolerated; esters, aryl chlorides and bromides were not. Furthermore, changing the steric bulk affected the enantioselectivity as well.

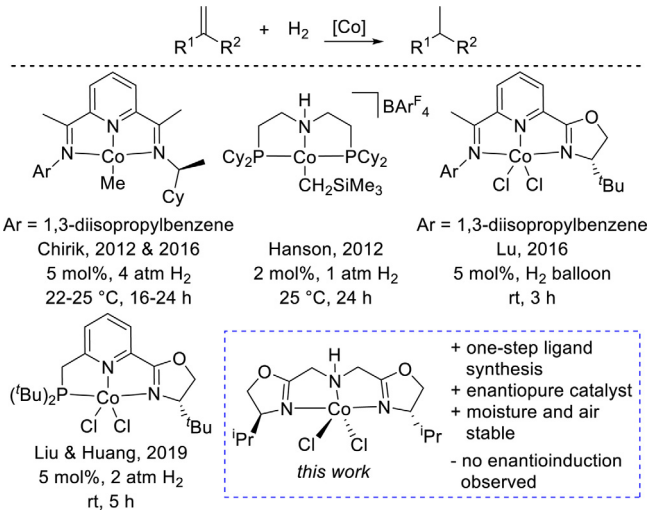
2. Results and discussion

2.1. Synthesis of catalyst

Despite these achievements, most of these systems involve multi-step syntheses to afford ligands and/or are moisture- and

* Corresponding author.
E-mail address: jones@chem.rochester.edu (W.D. Jones).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.poly.2020.114416
0277-5387/



Scheme 1. Cobalt-catalyzed alkene hydrogenation catalysts.

air-sensitive adding an additional amount of rigor to the hydrogenation reactions. Herein, we report a bench stable, novel, bisoxazoline ligated cobalt(II) dichloride complex utilizing a one-step synthesis to access enantioenriched ligand (Scheme 2). Starting with cheap and commercially available building blocks, treatment of iminodiacetonitrile with L-valine in the presence of $ZnCl_2$ afforded enantiopure ligand in 21% isolated yield. Reaction of enantiopure ligand with anhydrous Co(II) dichloride in THF at 40 °C (to improve solubility) afforded paramagnetic complex **1**. The ^{1}H NMR spectra of complex **1** show broadened and paramagnetically shifted resonances (See Supporting Information). Slow diffusion of ether into a THF solution containing **1** at −30 °C afforded a crystal suitable for X-ray structure determination (Fig. 1), which reveals a distorted trigonal bipyramidal geometry (τ_5 = 0.716) [28] around the cobalt center.

2.2. Hydrogenations with catalyst *1*

We began our investigation by examining the hydrogenation of 1,1-diphenylethylene (**2a**) catalyzed by a combination of bisoxazoline ligated cobalt complex **1** and reductant in a solution of toluene at room temperature under 1 atm of hydrogen. The use of sodium triethylborohydride as the reductant of choice resulted in 99% yield of hydrogenated product **3a** (Table 1, entry 1). Examination of alternative reducing agents did result in productive catalysis, however, poor conversion was observed (entry 2–3). Control reactions showed that without catalyst (entry 4) or reducing agent (entry 5), no product formation was observed.

With optimized reaction conditions, various alkenes were tested (Table 2). In general, these conditions proved to be general for a variety of alkenes with nonpolar and electron-donating groups, with electron withdrawing groups not being tolerated (See Supporting Information). Electron-donating groups such as methoxy (**3b**, **3g-h, 3m**, and **3p**) and a tertiary amine (**3c**) were well tolerated. Next, in order to assess steric hindrance a series of diarylethenes methylated in the ortho, meta, and para position were subjected to the optimized reaction conditions. Methylation of the meta (**3f**) and para (**3e**) position gave hydrogenated product, however, no product was observed upon *ortho*-methylation (See Supporting Information).

Applying these conditions to *N*-heterocyclic containing substrates proved to be successful (**3d** and **3 l**). Additionally, boron (**3i**) and ferrocene (**3j**) containing functional groups were tolerated. For substrates that showed diminished yields, increasing the catalyst loading (**3d** and **3i**) or adding electron-donating groups (**3 m**) did result in an increase in observed yield. The hydrogenation reaction was extended to substrates bearing cyclopentane (**3 g**) and cyclopropane (**3 h**) functional groups. Furthermore, internal alkenes were also tolerated as seen by products **3n, 3o,** and **3p**.

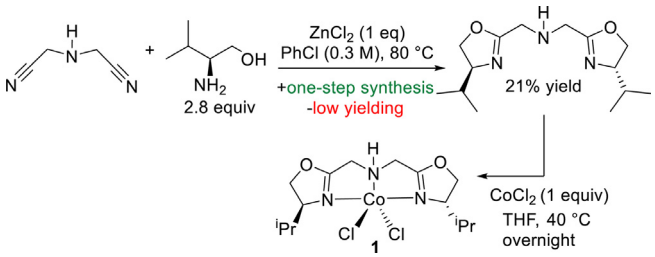
Strikingly, substrates with electron withdrawing groups shut down catalytic activity (See Supporting Information for all incompatible substrates). For example, 1,1-disubstituted olefins with chloro, bromo, CF_3, and CO_2Et substituents gave no hydrogenation products. Additional experiments were run to better understand why certain substrates are not tolerated by this system. **2a** and an incompatible substrate, 2-(1-phenylvinyl)thiophene, were added to the same reaction flask and subjected to the standard hydrogenation conditions previously described. No product formation of either substrate was seen, suggesting that catalyst inhibition, from substrate binding, could be the cause of this inactivity. Another competition reaction was run between **2a** and an incompatible substrate, 1-bromo-4-(1-phenylvinyl)benzene. Here it was seen that some product from hydrogenation of **2a**, 1,1-diphenylethane, had formed. This result suggests that the inability to hydrogenate alkenes with some electron-withdrawing groups is due to the substrates inhibiting the catalyst itself, either by coordination or by a chemical side-reaction (See Supporting Information).

It is also important to note that while complex **1** is enantiopure, no enantioinduction was observed in these hydrogenation reactions (1–5% e.e., see Supporting Information). The lack of enantioselectivity was surprising, in that hydroboration of arylethenes with a similar pyridine-oxazoline-cobalt catalyst proceeds with good enantioselectivity (up to 99% e.e.) [29]. Addition of a drop of mercury to the reaction with 1,1-diphenylethylene does not inhibit the reaction (quantitative hydrogenation), providing support for a homogeneous catalyst. However, examination of the filtrate at the end of the hydrogenation reaction by ^{1}H NMR spectroscopy shows the presence of free bis-oxazoline ligand. This observation could indicate that the true catalyst forms from ligand dissociation, but the mercury drop experiment argues against a nanoparticle catalyst. It is more likely that ligand loss follows from catalyst decomposition, as no species could be isolated or identified by reaction of **1** with $NaBEt_3H$. This methodology was extended to the gram scale synthesis of **3c** where a 90% isolated yield was achieved. The ability to apply this chemistry to a large scale highlights the practicality of this methodology (See Supporting Information).

3. Experimental

3.1. General information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Iminodiacetonitrile (Alfa Aesar) was recrystallized from ethyl acetate before use. All procedures and routine manipulations were performed under a nitrogen atmosphere (glovebox) or on a high-vacuum line using modified Schlenk techniques. Tetrahydrofuran (THF), toluene, ether, pentane, and dichloromethane (DCM) were obtained by from an Innovative Technology PS-MD-6 solvent purification system. Solvents were further degassed by 3–6 freeze-pump-thaw cycles and stored in a nitrogen-filled glovebox. ^{1}H and ^{13}C{^{1}H} NMR spectra were acquired on 400 and 500 MHz Bruker NMR instruments. NMR chemical shifts are reported in ppm and are referenced to the residual solvent peak for $CDCl_3$ (δ = 7.26 ppm, ^{1}H NMR; δ = 77.16 ppm, ^{13}C{^{1}H} NMR. Coupling constants (J) are reported in Hertz. GC–MS spectra were recorded on a Shimadzu QP2010 instrument with an SH-Rxi-5 ms column



Scheme 2. Synthesis and structure of complex **1**.

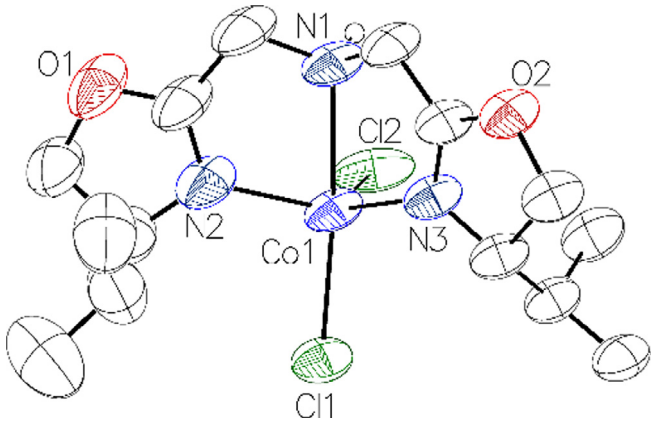
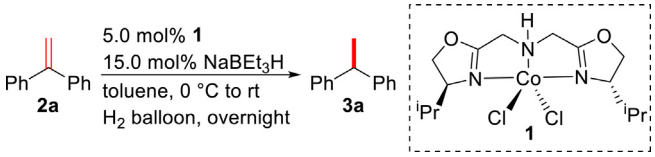


Fig. 1. Thermal ellipsoid plot (50%) of complex **1**.

Table 1
Optimization of reaction conditions.[a]



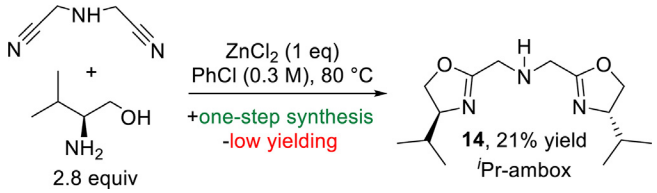
Entry	Change in conditions	**3a** (%)[b]
1	None	99[c,d]
2	15.0 mol% MeLi	70
3	15.0 mol% $LiCH_2SiMe_3$	36
4	No [Co]	0
5	No $NaBEt_3H$	0

[a] Reactions were run with 0.25 mmol **2a** in 0.5 mL of solvent.
[b] Yield determined via ^1H NMR spectroscopy vs 2,4,6-trimethylbenzaldehyde as internal standard.
[c] Isolated yield.
[d] Running the reaction with 2 equiv $NaBEt_3H$ gives the same yield as with 3 equiv.

(15 M × 0.25 mm ID × 0.25μ film). Column flow = 0.7 mL/min, temperature program: 3 min at 50 °C, then increase at 20 °C/min to 235 °C and hold for 3.5 min. Chromatography was performed on silica gel (EMD, silica gel 60, particle size 0.040–0.063 mm) using standard flash techniques. Products were visualized by UV. Enantiomeric excesses were analyzed by GC-FID using a Shimadzu GC-2010 gas chromatograph equipped with a FID detector, and a Cyclosil-B column (30 m × 0.25 mm × 0.25 μm film). Separation method: 1 μL injection, injector temperature: 240 °C, detector temperature: 300 °C. Gradient: column temperature set at 80 °C for 1 min, then to 240 °C at 16 °C/min for 4 min. Total run time: 15.0 min. Elemental analyses were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456. Microanalysis samples were weighed with a PerkinElmer Model AD6000 Autobalance and their compositions were determined with a PerkinElmer 2400 Series II Analyzer. For X-ray structures: data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B04 Hutchinson Hall, Department of Chemistry, University of Rochester (NSF MRI grant CHE-1725028).

3.2. Synthesis of bisoxazoline (ambox) ligand

(*S*)-2-amino-3-methylbutan-1-ol was synthesized from L-valine [30]. Bis(((*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl)methyl)amine was synthesized according to Gade's procedure [31].



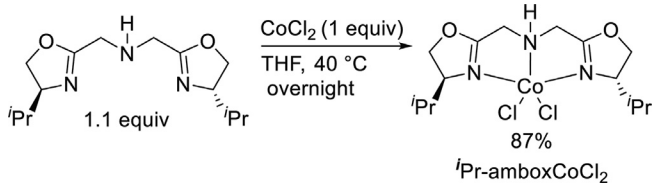
To an oven-dried 3-neck round bottom fitted with a stir bar was added $ZnCl_2$ (1.36 g, 1 equiv). The round bottom was capped with rubber septa and the system was placed under N_2 flow. Next, PhCl (30 mL, 0.34 M with respect to bisnitrile) was added and the reaction mixture was allowed to stir. Sequentially, amino alcohol (2.26 g, 2.8 equiv) and nitrile (0.950 g, 1 equiv) were added under positive flow of N_2. The reaction mixture was heated to 80 °C. Reaction completion was judged by TLC by monitoring the disappearance of starting material, this took about 24 h. NOTE: during the course of the reaction, polymerization of reagent(s) is observed, and this may result in stirring challenges. Upon completion, the reaction mixture was cooled, filtered through celite and concentrated *in vacuo* to afford a deep red oily residue. The oily residue was purified by flash chromatography (8:2 ethyl acetate: methanol) to afford **14** as a red oil in 21% yield.

^1H NMR (500 MHz, chloroform-*d*) δ 4.19 (t, *J* = 8.9 Hz, 2H), 3.90 (t, *J* = 8.1 Hz, 2H), 3.83 (q, *J* = 8.0 Hz, 2H), 3.44 (s, 4H), 1.67 (dp, *J* = 13.4, 6.7 Hz, 2H), 0.90 (d, *J* = 6.8 Hz, 6H), 0.81 (d, *J* = 6.7 Hz, 6H).

$^{13}C\{^1H\}$ NMR (126 MHz, chloroform-*d*) δ 165.13, 72.12, 70.27, 45.70, 32.58, 18.86, 18.18.

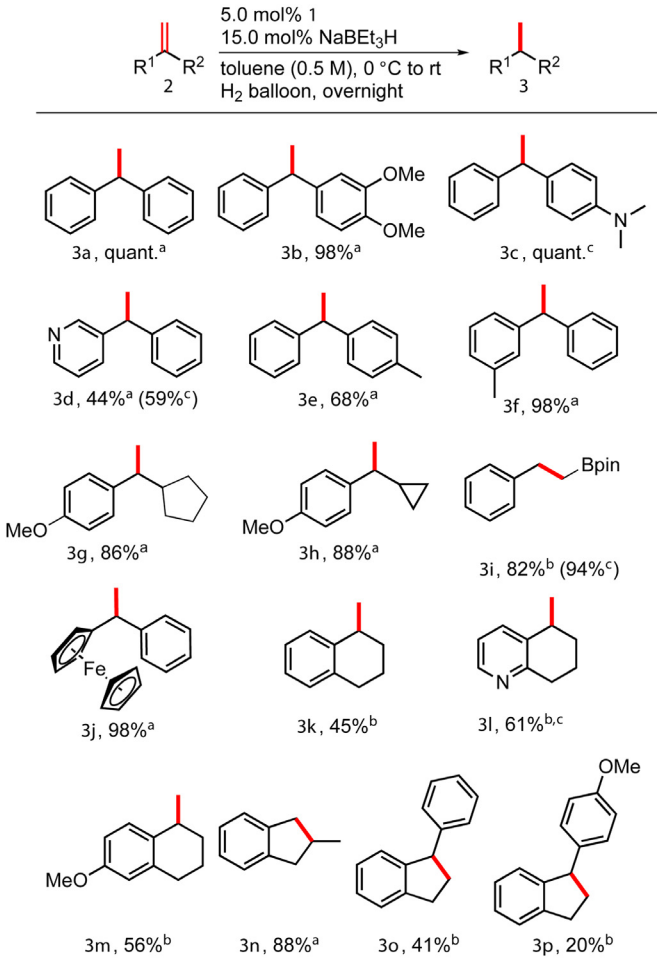
GC–MS: 267, 155, 141, 127, 114, 84, 70, 69, 55.

3.3. Synthesis of the cobalt complex ^{i}Pr-amboxCoCl$_2$



A 100 mL round-bottomed flask fitted with a Teflon coated stir bar was charged with anhydrous $CoCl_2$ (390 mg, 3.0 mmol, 1.0 equiv) followed by the addition of THF (30 mL). To the $CoCl_2$ solution was added bis(((*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl) methyl)amine (882 mg, 3.3 mmol, 1.1 equiv) in THF (5 mL), instantly turning the solution a dark color. The resulting mixture was heated to 40 ℃ and stirred overnight. A blue solid was precipitated by the addition of Et_2O (30 mL). The resulting mixture was filtered and the solid was washed with Et_2O to afford ^{i}Pr-amboxCoCl$_2$ (1.03 g, 2.6 mmol, 87% yield), a blue solid. Crystals suitable for X-ray diffraction were obtained by slow diffusion of ether into a THF solution at – 30 ℃.

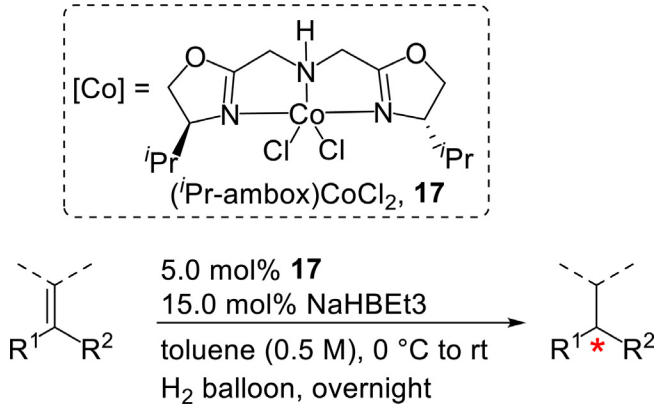
Table 2
Substrate scope of the hydrogenation reaction.



[a]Reactions were run with 0.25 mmol **2** in 0.5 mL of solvent. Isolated yield. [b]Reactions were run with 0.25 mmol **2** in 0.5 mL of solvent. Yield determined via ^{1}H NMR spectroscopy vs 2,4,6-trimethylbenzaldehyde as internal standard. [c]10.0 mol% **1**, 30.0 mol% $NaBEt_3H$.

Anal. Calcd for $C_{14}H_{25}Cl_2CoN_3O_2$: C, 42.33, H, 6.34, N, 10.58. Found: C, 42.12, H, 6.52, N, 10.44.

3.4. General procedure for the hydrogenation of alkenes [32]



For convenience, reactions were set up in a nitrogen-filled glove box.

An oven-dried 1-dram vial equipped with a Teflon-coated stir bar was charged with ^{i}Pr-amboxCoCl$_2$ (0.0125 mmol, 5.0 mg) and alkene (0.25 mmol). The vial was capped with a septum and brought outside the glovebox. Outside the glovebox, a balloon with hydrogen was added and the system was purged with H_2 three times. Next, toluene (0.5 mL) was added and the reaction mixture was cooled to 0 °C. To the cooled solution, $NaBEt_3H$ (1 M in toluene, 0.0375 mmol, 37.5 μL) (drop-wise addition) was added. Upon addition of $NaBEt_3H$, an immediate color change was observed from blue to brown. After complete addition, the reaction mixture was kept at 0 °C for *ca.* 5 min and then the ice bath was removed, and reaction mixture was stirred at room temperature overnight. Next, the reaction was quenched by the addition of pentane (2–3 mL). The mixture was filtered through a pad of celite, washed with pentane, and the filtrate was concentrated to afford crude material.

4. Conclusions

In conclusion, a novel bisoxazoline ligated cobalt complex was able to promote the hydrogenation of various alkenes under mild conditions. A variety of neutral, electron-donating, heterocyclic, and internal alkenes were able to readily undergo hydrogenation to give products in moderate to high yield while electron-withdrawing and sterically hindered substrates shut down the catalytic activity. Unfortunately, despite having an enantiopure catalyst, no enantioinduction was observed for the hydrogenation reactions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge funding from the U.S. Department of Energy (Grant. No. DE-SC0020230) for instrument usage and chemicals. A.M.P. acknowledges funding from an NSF GRFP award (DGE-1419118). M.D.R. was supported by an NSF grant (CHE-1762350). The NSF program is acknowledged for the purchase of an X-ray diffractometer (CHE-1725028).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2020.114416.

References

[1] A. Mukherjee, D. Milstein, Homogeneous catalysis by cobalt and manganese pincer complexes, ACS Catal. 8 (2018) 11435.
[2] L. Alig, M. Fritz, S. Schneider, First-row transition metal (De)hydrogenation catalysis based on functional pincer ligands, Chem. Rev. 119 (2019) 2681.
[3] W. Ai, R. Zhong, X. Liu, Q. Liu, Hydride transfer reactions catalyzed by cobalt complexes, Chem. Rev. 119 (2019) 2876.
[4] P.N. Rylander, Catalytic hydrogenation in organic synthesis, Academic Press, New York, 1979.
[5] P.G. Andersson, I.J. Munslow, Modern reduction methods, Wiley, New York, 2008.
[6] S.J. Roseblade, A. Pfaltz, Iridium-catalyzed asymmetric hydrogenation of olefins, Acc. Chem. Res. 40 (2007) 1402.
[7] J.J. Verendel, O. Pamies, M. Dieguez, P.G. Andersson, Asymmetric hydrogenation of olefins using chiral Crabtree-type catalysts: scope and limitations, Chem. Rev. 114 (2014) 2130.
[8] R. Crabtree, Iridium compounds in catalysis, Acc. Chem. Res. 12 (1979) 331.
[9] H. Yang, E. Wang, P. Yang, H. Lv, X. Zhang, Pyridine-directed asymmetric hydrogenation of 1,1-diarylalkenes, Org. Lett. 19 (2017) 5062.
[10] J.A. Osborn, F.H. Jardine, J.F. Young, G. Wilkinson, The preparation and properties of tris(triphenylphosphine)halogenorhodium(I) and some

reactions thereof including catalytic homogeneous hydrogenation of olefins and acetylenes and their derivatives, J. Chem. Soc. A. 1711 (1966).
[11] M. Biosca, M. Magre, M. Coll, Alternatives to phosphinooxazoline (t-BuPHOX) ligands in the metal-catalyzed hydrogenation of minimally functionalized olefins and cyclic β-enamides, Adv. Synth. Catal. 359 (2017) 2801.
[12] J. Louie, C.W. Bielawski, R.H. Grubbs, Tandem catalysis: the sequential mediation of olefin metathesis, hydrogenation, and hydrogen transfer with single-component Ru complexes, J. Am. Chem. Soc. 123 (2001) 11312.
[13] Y. Blum, D. Czarkie, Y. Rahamim, Y. Shvo, (Cyclopentadienone)ruthenium carbonyl complexes - a new class of homogeneous hydrogenation catalysts, Organometallics 4 (1985) 1459.
[14] H.M. Lee, D.C. Smith, Z. He, E.D. Stevens, C.S. Yi, S.P. Nolan, Catalytic hydrogenation of alkenes by the ruthenium–carbene complex HRu(CO)Cl (PCy3)(IMes) (IMes = Bis(1,3-(2,4,6-trimethylphenyl)imidazol-2-ylidene), Organometallics 20 (2001) 794.
[15] M.W. van Laren, C.J. Elsevier, Selective homogeneous palladium(0)-catalyzed hydrogenation of alkynes to (Z)-alkenes, Angew. Chem. Int. Ed. 38 (1999) 3715.
[16] Q.A. Chen, Z.S. Ye, Y. Duan, Y.G. Zhou, Homogeneous palladium-catalyzed asymmetric hydrogenation, Chem. Soc. Rev. 42 (2013) 497.
[17] P.J. Chirik, Iron- and cobalt-catalyzed alkene hydrogenation: catalysis with both redox-active and strong field ligands, Acc. Chem. Res. 48 (2015) 1687.
[18] G. Zhang, K.V. Vasudevan, B.L. Scott, S.K. Hanson, Understanding the mechanisms of cobalt-catalyzed hydrogenation and dehydrogenation reactions, J. Am. Chem. Soc. 135 (2013) 8668.
[19] Naveen Kulkarni, William D. Jones, Chemistry of Mn and Co Pincer Compounds, in: D. Morales-Morales (Ed.), Pincer Compounds: Chemistry And Applications, Elsevier, 2018, pp. 491–516.
[20] G. Zhang, B.L. Scott, S.K. Hanson, Mild and homogeneous cobalt-catalyzed hydrogenation of C=C, C=O, and C=N bonds, Angew. Chem. Int. Ed. 51 (2012) 12102.
[21] G. Zhang, Z. Yin, J. Tan, Cobalt(ii)-catalysed transfer hydrogen tion of olefins, RSC Adv. 6 (2016) 22419.
[22] K. Tokmic, C.R. Markus, L. Zhu, A.R. Fout, Well-defined cobalt(I) dihydrogen catalyst: experimental evidence for a Co(I)/Co(III) redox process in olefin hydrogenation, J. Am. Chem. Soc. 138 (2016) 11907.
[23] Y. Ogho, S. Takeuchi, Y. Natori, J. Yoshimura, Asymmetric reactions. X. Asymmetric hydrogenation catalyzed by bis(dimethylgly-oximato)cobalt(II)-chiral cocatalyst (amino alcohol) system, J Bull. Chem. Soc. Jpn. 54 (1981) 2124.
[24] U. Leutenegger, A. Madin, A. Pfaltz, Enantioselective reduction of α, β-unsaturated carboxylates with NaBH4 and catalytic amounts of chiral cobalt semicorrin complexes, Angew. Chem. Int. Ed. Engl. 28 (1989) 60.
[25] M.R. Friedfeld, M. Shevlin, G.W. Margulieux, L.C. Campeau, P.J. Chirik, 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. 138 (2016) 3314.
[26] J. Chen, C. Chen, C. Ji, Z. Lu, Cobalt-catalyzed asymmetric hydrogenation of 1,1-diarylethenes, Org. Lett. 18 (2016) 1594.
[27] Z. Zuo, S. Xu, L. Zhang, L. Gan, H. Fang, G. Liu, Z. Huang, Cobalt-catalyzed asymmetric hydrogenation of vinylsilanes with a phosphine–pyridine–oxazoline ligand: synthesis of optically active organosilanes and silacycles, Organometallics 38 (2019) 3906.
[28] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen–sulphur donor ligands; the crystal and molecular structure of aqua [1,7-bis(N-methylbenzimidazol-2′-yl)-2,6-dithiaheptane]copper(II) perchlorate, J. Chem. Soc. Dalton Trans. 1349 (1984).
[29] L. Zhang, Z. Zuo, X. Wan, Z. Huang, Cobalt-catalyzed enantioselective hydroboration of 1,1-disubstituted aryl alkenes, J. Am. Chem. Soc. 136 (2014) 15501.
[30] D.C. Crowley, D. Lynch, A.R. Maguire, Copper-mediated, heterogeneous, enantioselective intramolecular Buchner reactions of α–diazoketones using continuous flow processing, J. Org. Chem. 83 (2018) 3794.
[31] C. Mazet, L.H. Gade, Charging and deforming the pybox ligand: enantiomerically pure double helices and their interconversion, Chem. Eur. J. 8 (2002) 4308.
[32] Method taken from: Z. Zuo, S. Xu, L. Zhang, L. Gan, H. Fang, G. Liu, Z. Huang, Cobalt-catalyzed asymmetric hydrogenation of vinylsilanes with a phospine-pyridine-oxazoline ligand: synthesis of optically active organosilanes and silacycles Organometallics 38 (2019) 3906.