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Homogeneous Catalysis

Cobalt–Pincer Complexes in Catalysis

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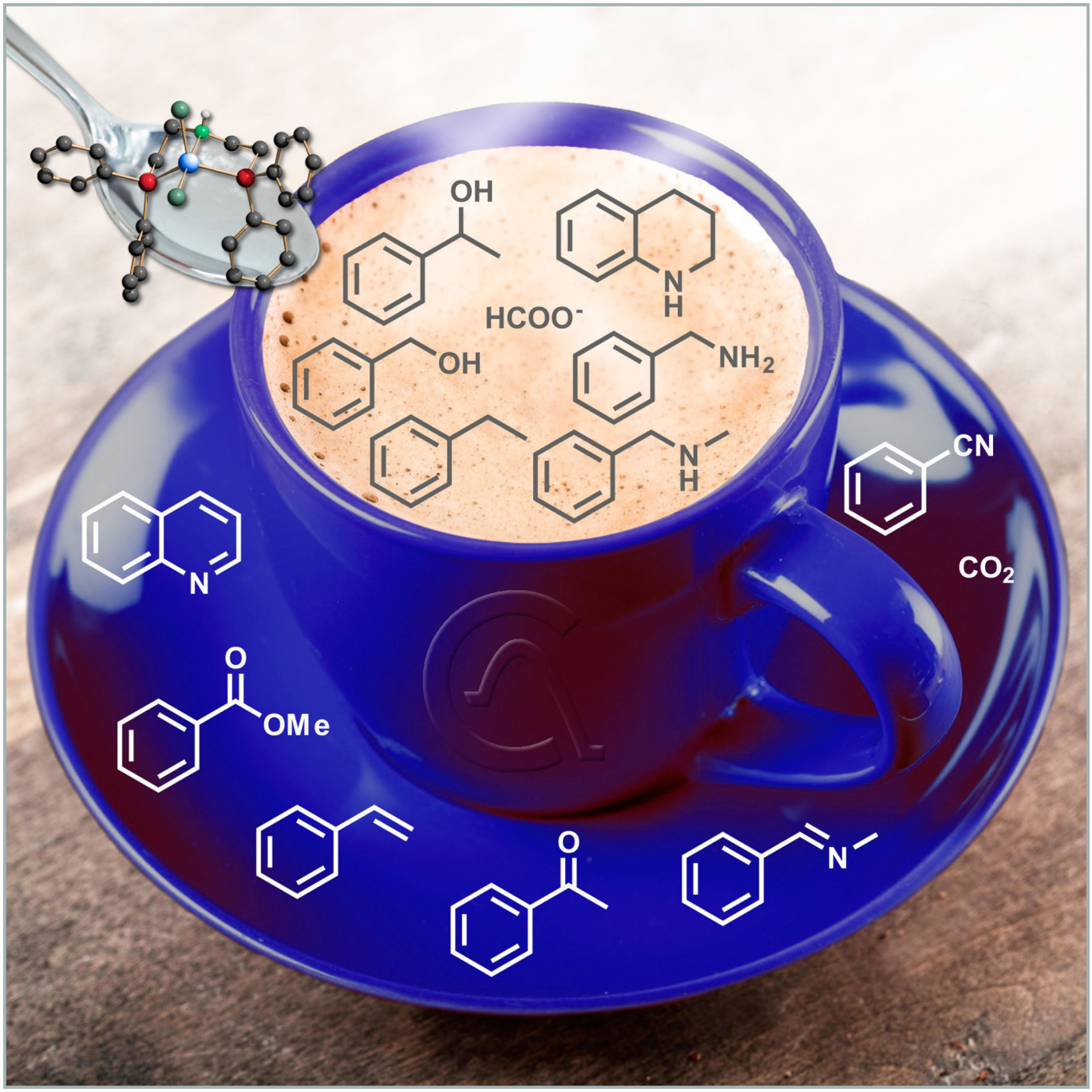


Abstract: Non-noble metal catalysts based on pincer type compounds are of special interest for organometallic chemistry and organic synthesis. Next to iron and manganese, currently cobalt–pincer type complexes are successfully applied in various catalytic reactions. In this review the recent progress in (de)hydrogenation, transfer hydrogenation, hydroboration and hydrosilylation as well as dehydrogenative coupling reactions using cobalt–pincer complexes is summarised.

1. Introduction

The term pincer ligands emerged in the late 1970s based on the pioneering studies by the groups of Shaw[1] and van Koten.[2] Pincer complexes are easily formed by complexation of a tridentate ligand with the central metal atom in a typical meridional geometry (Figure 1). This special ligand arrangement causes high thermal and chemical stability avoiding dissociation of the metal. Simple steric and electronic variations of the ligand motif allow a fine-tuning of chemical properties of these organometallic compounds and make them versatile for any catalytic reactions. The most common modifications are variations in the ring size (five or six membered rings) and the ring nature (aromatic vs. non-aromatic ring or elimination of the ring). Here, slight changes in the structure of the ligand often lead to noteworthy effects on selectivity and catalyst activity.[3]

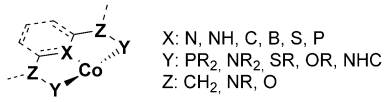
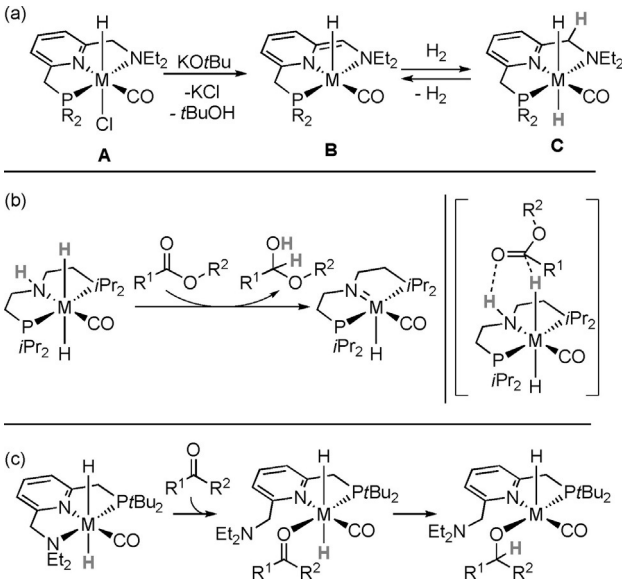


Figure 1. General structure of cobalt–pincer complexes.

Interestingly, in pincer complexes the ligand can actively participate in catalysis. Depending on the mechanism of the catalytic transformation, different activation modes are known (Scheme 1). In an outer sphere mechanism metal ligand cooperation (MLC) can occur, for example, through amine/amide mode or though the aromatisation/dearomatisation process without an overall change of the metal oxidation state.[4] As shown in Scheme 1a, in this aromatisation/dearomatisation process of the pyridine backbone a chemical bond, for example, H–OR, H–NR_2, H–C, can be activated by dearomatised complex **B** resulting in rearomatisation (**C**) through metal–ligand cooperation. Notably, the dearomatisation/deprotonation from **A** to **B** takes place in the presence of a base. In case of aliphatic pincer ligands in the backbone as presented in Scheme 1b, usually an outer-sphere mechanism is proposed via an amine/amide mode. In contrast, when the M–Y bond of pincer complexes, for example, during ketone hydrogenation (see Scheme 1c) is cleaved, the reaction runs by means of an inner-sphere mechanism.



Scheme 1. a) Dearomatisation/aromatisation of pyridine-based pincer complexes. b) Outer-sphere mechanism. c) Ketone hydrogenation through metal–N cleavage.

Based on the above-mentioned advantages, pincer-based complexes have been emphasised as a privileged class of compounds with broad applications in homogeneous catalysis.[5] The organometallic chemistry of noble-metal–pincer complexes such as ruthenium,[6] iridium[7] or palladium[8] and their catalytic reactions have been published in comprehensive books and reviews.

In this context, non-noble metal catalysis including the use of iron, nickel, manganese or molybdenum-derived pincer-type catalysts is on the march.[9] Here, also cobalt-derived pincer complexes attracted interest as cheap, abundant and biocompatible alternative for catalytic applications.[10] The first catalytic application of cobalt–pincer complexes derived from bis(imino)pyridine scaffold was discovered independently by Brookhart, Bennett and Gibson in 1998.[11] For a long time, these complexes have been regarded as suitable catalysts for olefin polymerisation and oligomerisation reactions.[12]

A change of thinking was initiated by the seminal work of Hanson, who presented cobalt-based complexes for the hydrogenation of alkenes, imines as well as ketones and aldehydes.[13,14] In addition, the recent progress of cobalt–pincer type catalysis was promoted by the successful advancements

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of iron– and manganese–pincer-based catalysts.[9,15] Here, the recent development of cobalt–pincer compounds regarding their application in homogeneous catalysis especially for (de)-hydrogenation, transfer hydrogenation, hydroboration and hydrosilylation, as well as dehydrogenative coupling reactions, will be discussed and summarised.

2. Catalytic Reduction

2.1 Catalytic hydrogenation

The hydrogenation of carbon–carbon multiple bonds is one of the most extensively employed catalytic reactions in the pharmaceutical industry and for the synthesis of fine chemicals and commodities.[16] For decades, homogeneous catalysis focused on the improvements in this field and recently also the chemistry of Co–pincer complexes contributed to this goal.

The Caulton group described one of the first Co–pincer complexes for hydrogen activation.[17] Although complex **1** is able to activate H_2, the reduction of ethene runs only in a stoichiometric mode due to the steric bulkiness of **1** (Figure 2).

Inspired by previous studies on the redox active diimine pyridine ligands[18] and their successful application of cobalt–diimine–pyridine complexes in polymerisation,[19] Budzelaar and co-workers tested the Co–pincer complexes $(NNN^{dip})CoCH_2SiMe_3$ (**2a**) and $(NNN^{hex})CoCH_2SiMe_3$ (**2b**) in the hydrogenation of olefins.[20] The reaction of **2a** with H_2 produces a diamagnetic species, which is postulated as a hydride (NNN)CoH complex. In stoichiometric experiments insertion of the olefin into the Co–H bond was demonstrated forming the corresponding alkyl derivative. Upon addition of hydrogen, the trimethylsilyl methyl ligand is hydrogenated to the corresponding tetramethylsilane and the hydride species is regenerated. As a more convenient strategy the activation of $(NNN)CoCl_2$ with TIBA (triisobutylaluminum) in order to establish an in situ catalyst system provided similar results to the use of **2a**,**b**.

Significant contributions to understand the role of redox-active chelates in base metal catalysis have been made by the group of Chirik. Due to the precedent works[18d,19a,21] they developed cobalt catalysts that are among the most active for hydrogenation of olefins including enantioselective reactions. For example, the complex $(^{iPr}CNC)CoCH_3$ (**3**) was successfully explored for the hydrogenation of tri- and tetra-substituted non-activated alkenes, such as *trans*-methyl stilbene, 1-methyl-

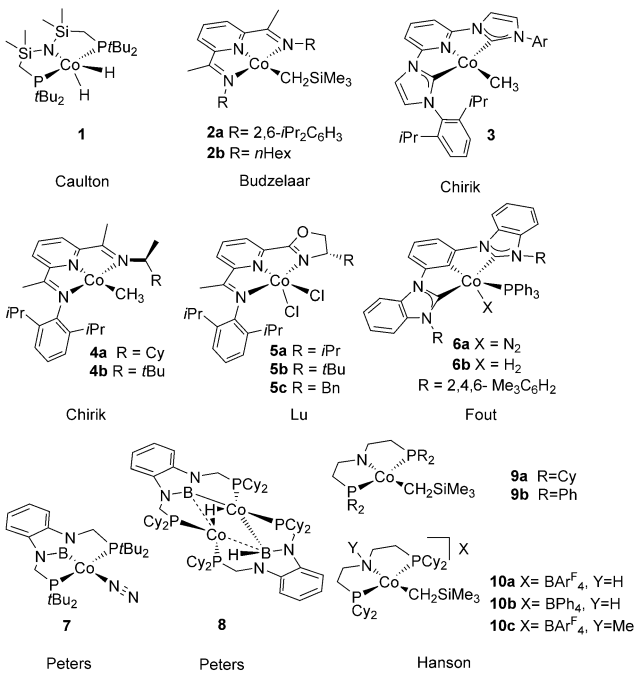


Figure 2. Cobalt–PNP-pincer complexes applied in olefin hydrogenation.

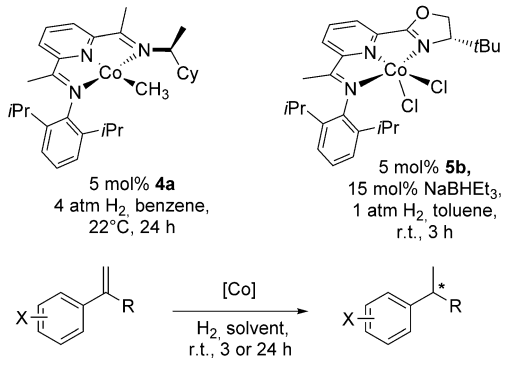
Kathrin Junge received her PhD degree in Chemistry from the University of Rostock in 1997 working with Prof. E. Popowski. After a postdoctoral position in the Max-Planck group of Uwe Rosenthal, she joined the group led by Matthias Beller in 2000. Since 2008 she has been the group leader for homogeneous redox catalysis at LIKAT. She has been involved for years in catalysis research, where she has developed efficient catalytic hydrogenations for ketoesters and for other carbonyl compounds including carboxylic acid derivatives. Moreover, she created several new ligands, especially for hydrogenation reactions. Her current main interest is the development of environmentally benign and efficient catalytic reactions based on inexpensive, non-precious metals.

Veronica Papa studied chemistry at the University of Naples "Federico II". She received her Master's degree in July 2015 under the guidance of Prof. F. Ruffo. Afterwards, she joined the group of Prof. Matthias Beller at LIKAT in Rostock starting with her PhD. Her research focuses on homogeneous hydrogenations with non-noble metals, especially Co and Mn.

Matthias Beller studied chemistry at the University of Göttingen, Germany, where he completed his PhD thesis in 1989 in the group of L.-F. Tietze. As recipient of a Liebig scholarship, he then spent one-year with K. B. Sharpless at MIT, USA. From 1991 to 1995, Beller worked in the industry. Then, he became Professor at the TU Munich. In 1998, he relocated to Rostock to head the Institute for Organic Catalysis, which became the Leibniz-Institute for Catalysis. He has received several awards including the Otto Roelen Medal, the Leibniz Prize, the Emil Fischer Medal and the Karl Ziegler-Prize, the first "European Prize for Sustainable Chemistry", the "Paul Rylander Award" of the Organic Reaction Catalysis Society of the USA and the Gay-Lussac-Alexander-von-Humboldt-Prize of the French Academy of Sciences. He was named "Entrepreneur of the Year" of Rostock and he received the German Federal Cross of Merit. Matthias Beller is also Vice President of the Leibniz Association and a member of three German Academies of Sciences including the German National Academia "Leopoldina".

1-cyclohexene and 2,3-dimethyl-2-butene, under very mild conditions.[22] A stereoselective version was achieved by suitable modification of the ligand architecture. Here, the Co–pincer complexes **4a**,**b** contain one imine moiety substituted with large aryl ring and another one bearing a chiral amine group.[23a] During the organometallic studies of this complex, it has been noted that the cyclometalation of the chiral element (alkylimine arm) is competitive with the formation of the cobalt hydride, which has a detrimental effect on the catalytic activity. In general, the highest selectivity and conversion have been achieved with less hindered alkenes and electron-rich styrenes. The arylated alkenes have been hydrogenated with *ee* values of 80–98% and the more crowded olefins showed the highest selectivity, albeit with lower conversion (Table 1). Notably, the values of enantiomeric excess obtained in this manuscript are among the highest *ee* values that were reported in the literature for the hydrogenation of alkenes.

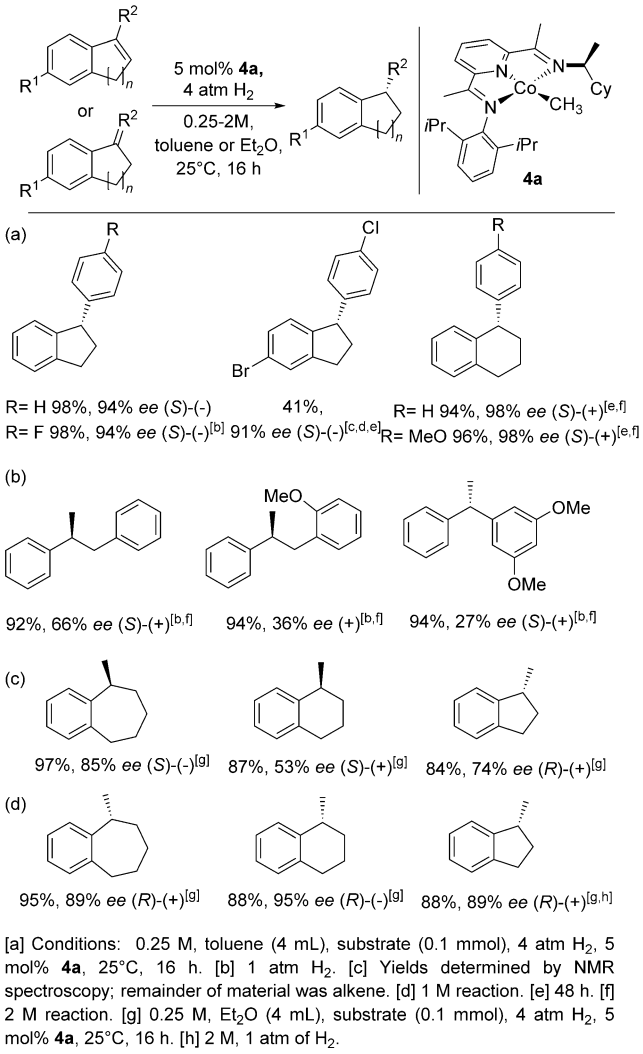
Table 1. Asymmetric hydrogenation of selected olefins using Co-catalysts **4a**[a] or **5b**.[b]



Entry	X	R	Yield [%]	*ee* [%]
1	H	*i*Pr	87	**4a**: 90 (*R*)
2	H	*t*Bu	5	**4a**: 98 (*R*)
3[c]			99	**5b**: 91 (*R*)
4	4-NMe_2	*i*Pr	>98	**4a**: 96 (*R*)
5	4-MeO	*i*Pr	>98	**4a**: 94 (*R*)
6[c]	4-MeO	Et	>99	**5b**: 91 (*R*)
7	4-F	*i*Pr	>98	**4a**: 78 (*R*)
8	2-Cl	Ph	99	**5b**: 90 (*S*)
9	2-Cl	3-CF_3-Ph	>99	**5b**: 99 (*S*)
10	2-Cl	3-MeO-Ph	>99	**5b**: 95 (*S*)

[a] Conditions: Substrate (0.1 mmol), 5 mol% **4a**, benzene (1 mL), 24 h. [b] Conditions: Substrate (0.5 mmol), 5 mol% **5b**, 15 mol% $NaBHEt_3$, toluene (1 mL), 3 h. [c] 1 h. Yields determined by GC.

A similar strategy for the development of chiral Co pincer catalysts **5a**–**c** for the enantioselective hydrogenation of alkenes was applied by the group of Lu, when they modified the iminopyridine ligand backbone with the oxazoline moiety.[23b] The bench-stable Co pincer complex **5b** was successfully applied for the asymmetric reduction of 1,1-diarylethenes after activation with $NaBHEt_3$ and showed a unique O-chloride effect with high enantioselectivities up to 99% *ee* (Table 1, entries 8–10). Additionally, α-alkylstyrenes were efficiently reduced within 1 hour using Co catalyst **5b** (Table 1, entries 3 and 6).



[a] Conditions: 0.25 M, toluene (4 mL), substrate (0.1 mmol), 4 atm H_2, 5 mol% **4a**, 25°C, 16 h. [b] 1 atm H_2. [c] Yields determined by NMR spectroscopy; remainder of material was alkene. [d] 1 M reaction. [e] 48 h. [f] 2 M reaction. [g] 0.25 M, Et_2O (4 mL), substrate (0.1 mmol), 4 atm H_2, 5 mol% **4a**, 25°C, 16 h. [h] 2 M, 1 atm of H_2.

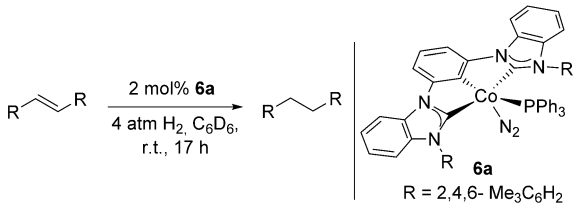
Scheme 2. Selected examples of asymmetric hydrogenation of a) functionalised cyclic olefins and b) 1,1-disubstituted alkenes using Co catalyst **4a**.[a] Examples for enantioselective hydrogenation of isomeric c) *exo*- and d) *endo*-cyclic alkenes using Co catalyst **4a**.[g]

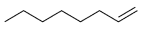
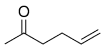
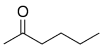
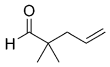
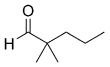
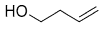
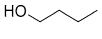
Furthermore, Chirik and co-workers explored the catalytic activity of **4a** for asymmetric hydrogenation of functionalised cyclic olefins and 1,1-disubstituted alkenes (Scheme 2).[24] It should be highlighted that (*S*)-1-*p*-methoxyphenyl-1,2,3,4-tetrahydronaphthalene is produced in 98% *ee*, while in a previous study this substrate was obtained by Ir-catalyst in 96% *ee*.[25] Additionally, Co–pincer complex **4a** displayed excellent performance for reduction of 1,1-diaryl ethenes and related alkenes, although with decreased enantioselectivities. The stereocontrol in the bis(imino)pyridine cobalt catalyst **4a** has been further investigated in the asymmetric hydrogenation of isomeric *exo*- and *endo*-cyclic alkenes. Comparing seven-, six- and five-membered cyclic olefins varying enantioselectivities were observed as a function of alkene position and ring size. It was suggested, that for some alkenes the isomerisation can be competitive or faster than the hydrogenation.

This fact was analysed in more detail by Hopmann, who performed a comprehensive quantum mechanical analysis concerning the catalytic performance of **4a**.[26] Based on these theoretical studies, the conflict between isomerisation and hydrogenation pathway was illuminated. A key finding was that **4a** catalyses a competing alkene isomerisation reaction, which has crucial implications for the yield and the stereochemical outcome of alkene hydrogenation.

The catalytic activity of (^{Mes}CCC)CoI(N_2)(PPh_3) **6a** was tested in the reduction of styrene at room temperature.[27] At the end of the reaction (2 h), the dihydrogen species **6b** was detected as a resting state of the catalytic cycle. This is probably the first case in which a well-defined homogeneous cobalt–dihydrogen complex has been used as an effective hydrogenation catalyst. The applicability of this method has been evaluated with more hindered alkenes, tolerating functionalities such as hydroxyl groups, ketones, anhydrides and aldehydes (Table 2). The selectivity toward terminal alkenes over internal alkenes was achieved tuning the reaction conditions.

Table 2. Hydrogenation of selected alkenes using Co-catalyst **6a**.[a]



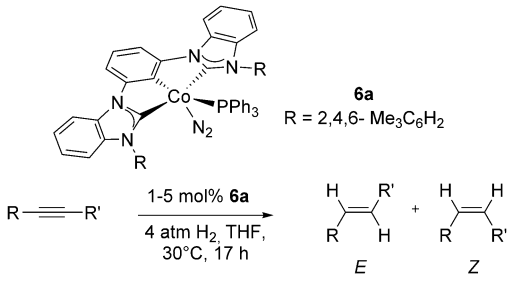
Entry	Substrate	Product	Conv. [%]	*t* [h]
1			>99	3
2			>99	2
3			>99	22
4			>99	2
5[b]			>99	2

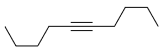
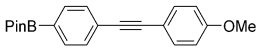
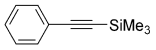
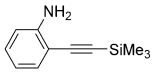
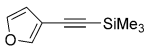
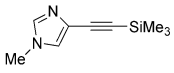
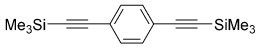
[a] Conversion was monitored by ^{1}H NMR spectroscopy. [b] Alkane product obtained after heating to 60°c for 19 h.

An additional application of **6b** was demonstrated in the semihydrogenation of alkynes (Table 3).[28] At low temperatures (30 °C) the complex (^{Mes}CCC)CoI(N_2)(PPh_3) **6a** is able to reduce a broad range of alkynes with high selectivity to *trans*-alkenes. In this process a variety of functional groups are well tolerated in *para* as well as in *ortho* position. Substituted diphenylacetylenes can be hydrogenated with high yield and *E*/*Z* ratio both with electron-donating and -withdrawing groups. Furthermore, a substrate with two internal alkyne moieties was smoothly transformed (Table 3, entry 7). Mechanistic studies indicated that first *cis*-hydrogenation occurred followed by a *trans*-isomerisation to yield the corresponding *E*-alkenes.

As shown in Table 4, also the Co–pincer complex **7** reduced 1-octene and styrene to the corresponding alkanes under very

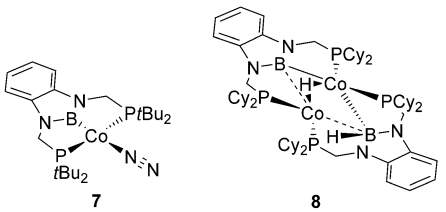
Table 3. Semihydrogenation of selected alkynes using Co-catalyst **6a**.[a]

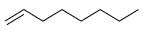


Entry	Substrate	Yield (conv.) [%]	*E*:*Z*
1		69 (>99)	81:19
2		86 (89)	>99
3		59 (>89)	99:1
4		96 (97)	99:1
5		64 (87)	>99
6		83 (92)	>99
7		66 (95)	*E*,*E*:*Z*,*Z* >99

[a] Conditions: Substrate (0.1 mmol), 1–5 mol% **6a**, THF (4 mL). Isolated yields are in average of duplicate runs and conversion to alkene is listed in parentheses. [b] *T* = 90 °C, 1 atm H_2.

Table 4. Catalytic olefin hydrogenation with **7** and **8**.[a]



Entry	Olefin	TOF **7** [h^{-1}] (Yield [%])	TOF **8** [h^{-1}] (Yield [%])
1		1000 (100)	2.5 (100)
2		1000 (92)	8 (100)
3		–	4 (100)
4		–	5 (100)

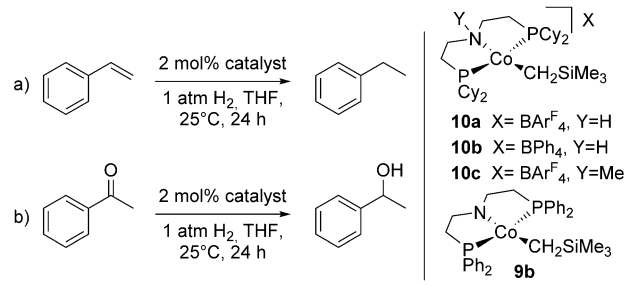
[a] Conditions: r.t., 1 atm H_2, C_6D_6, 2 mol% catalyst. The yields were determined by NMR spectroscopy using 1,3,5,-trimethoxybenzene as internal standard. The turnover frequency (h^{-1}) was calculated when the starting olefin was not detectable.

mild conditions (2 mol% **7**, 3 min, r.t., 1 atm H_2) and with a TOF = 1000 h^{-1}, while the reduction of internal alkenes was achieved with the bimetallic derivative **8** bearing cyclohexyl substituents on the chelating phosphorus atoms.[29] A comparison of the catalytic efficiency of the monomeric **7** and the dimeric complexes **8** showed a lower activity for the latter one. DFT calculations regarding the mechanism predicted the formation of (^{tBu}PNBNP)Co(H)$_2$ as catalytic active species and the rate-determining barrier for the hydrogenation of styrene of 17.3 kcal mol^{-1}.[30]

In 2012 and 2013, Hanson's group reported Co–PNP-pincer complexes, which are able to hydrogenate alkenes, imines as well as ketones and aldehydes.[13,14] At room temperature using 2 mol% **10a** or a combination of 2 mol% **9a** and H[BAr^F_4](Et_2O)$_2$ and 1 bar of H_2 aromatic and aliphatic alkenes were reduced within 24–40 hours giving yields between 80–100%. In order to study the functional group tolerance, more challenging substrates have been tested such as 4-pentenoic acid to furnish pentanoic acid.

Hanson and co-workers investigated the metal–ligand cooperative interaction and the possible involvement of the N–H group in the catalytic mechanism in detail (Table 5).[14] Additionally they evaluated the variation of the substituents on the chelating phosphorus atoms and the impact of the counterion replacing BAr^F_4 with BPh_4. For this purpose, the related complexes [(PNHP^{Cy})Co^{II}(CH_2SiMe_3)]BPh_4 (**10b**), [(PNHMeP^{Cy})Co^{II}-(CH_2SiMe_3)]BAr^F_4 (**10c**) and (PNP^{Ph})Co^{II}(CH_2SiMe_3) (**9b**) were prepared and tested in the hydrogenation of styrene (Table 5, reaction a). The phenyl-substituted derivative **9b** (used with H[BAr^F_4]·(Et_2O)$_2$ to form in situ the active pre-catalyst) is not active compared to the cyclohexyl substituted **10a** showing the detrimental effect of substituent on the phosphorous moiety. A comparison of **10a** and **10b** demonstrated that the counterion has no significant influence on the catalytic activity regarding the hydrogenation of styrene. Similarly, no differences have been detected between Co PNP complex **10a** and the N-methylated species **10c**, indicating that the cooperative interaction involving N–H group on the chelating ligand is not crucial in olefin hydrogenation.

Table 5. Comparison of Co pre-catalysts for the hydrogenation of styrene and acetophenone.[a]



Entry	Catalyst	Yield [%] (path a)[b]	Yield [%] (path b)[c]
1	**10a**	(>99)	(89)
2	**10b**	(>99)	(35)
3[d]	**10c**	(>99)	0
4[d]	**9b** + H[BAr^F_4]·(Et_2O)$_2$	0	0

[a] Conditions: Substrate (0.5 mmol), catalyst (2 mol%), THF (2 mL). [b] Yields determined by GC-FID. [c] Isolated Yields. [d] The hydrogenation of acetophenone is performed at $T = 60\,^{\circ}C$.

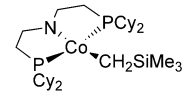
The mechanism predicted for these reactions is coherent with previous work by Budzelaar et al.[20] and much evidence supported a Co^{II} valence during the catalytic cycle as the active species. Regarding this mechanism, Yang and co-workers provide computational studies to reinforce these predictions.[31] They analysed the hydrogenation of propylene in the presence of [(PNMeP^{iPr})Co^{II}(CH_2SiMe_3)][BAr^F_4] (**10d**) and calculated a value of 24.8 kcal mol^{-1} for the rate determining step of the H_2 splitting. Furthermore, they found that the energy barrier for the exchange of H with Me on the N atom is increased by 1.9 kcal mol^{-1}.

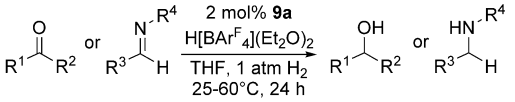
Compound **9a** is also an active catalyst for the hydrogenation of ketones, aldehydes and imines (Table 6). Until now, hydrogenation of imines was scarcely investigated with cobalt-based catalysts.[32] Hanson and colleagues provided three examples for imine reduction showing yields between 65–88% (Table 6, entries 10–12). The hydrogenation of ketones and aldehydes by catalyst **9a** has been investigated with a broader number of substrates. Under mild conditions (1 atm of H_2, 25–60 °C, 2 mol% **9a**, 24 h) the reactions proceeded in nearly quantitative yield for both types of carbonyl compounds demonstrating tolerance of several functional groups. Thus, in *N*-methyl-4-piperidone the amine moiety is not affected during the reaction (entry 4). In a competition experiment using a mixture 1:1 of benzaldehyde and styrene, the hydrogenation of benzaldehyde was completed while only 16% of styrene was reduced at room temperature by complex **9a** after 24 h. In order to gain insight into the mechanism for C=O reduction, complex [(PNMeP^{Cy})Co^{II}(CH_2SiMe_3)][BAr^F_4] (**10c**) was tested in the hydrogenation of acetophenone and showed no activity (Table 4, entry 3, reaction b). This result indicates that a metal ligand bifunctional pathway takes place where the N–H moiety of the ligand participates in the catalytic cycle.

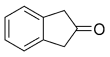
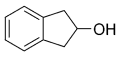
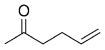
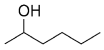
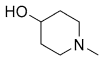
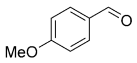
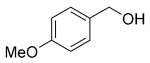
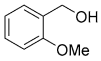
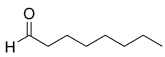
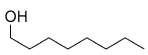
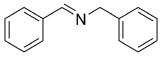
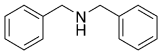
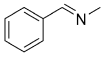
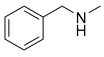
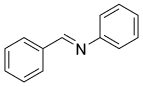
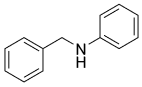
In 2015, Kempe's group presented a family of novel Co–pincer catalysts **11a–c** and **12a–c** that was tested in the hydrogenation of acetophenone (Scheme 3).[33] A comparison between **11** and **12** showed a beneficial effect of the triazine ring for the catalytic efficiency. The most active Co–PN_5P complex **11a** (0.25–0.5 mol%) was able to hydrogenate a wider range of aryl–alkyl, diaryl, and aliphatic ketones under mild conditions with good tolerance for several functional groups. Unique selectivity of C=O bonds in the presence of C=C bonds has been noticed, which is inverse to that of Hanson's catalyst.[14] The pre-catalyst is activated through salt elimination, adding two equivalents of a base (NaO*t*Bu).

In Figure 3, three different Co–pincer catalyst systems for the hydrogenation of carboxylic acid esters are shown in chronological order. Each contribution represents an improvement regarding the applied reaction conditions and the substrate scope.

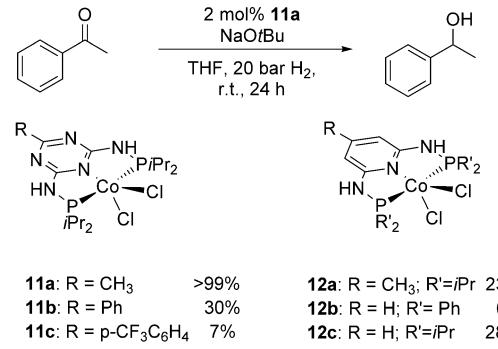
Table 6. Selected examples of ketones, aldehydes and imine hydrogenation using Co-catalyst **9a**.[a]





Entry	Substrate	Product	*t* [h]	Yield [%][f] (NMR)[g] {GC}[h]
1			24	89 (98)
2[b]			48	97 (99)
3[c]			65	{99}
4			65	{66}
5			24	86 (92)
6			24	96 (>99)
7[d]			24	92 (98)
8[d]			24	91 (99)
9[e]			64	92 (>99)
10[e]			42	84 (89)
11[e]			72	88 (98)
12[e]			48	65 (70)

[a] Conditions: Substrate (0.5 mmol), THF (2 mL), H_2 (1 atm), 25 °C. [b] *T* = 60 °C. [c] *T* = 25 °C, H_2 (4 atm). [d] *T* = 50 °C. [e] *T* = 60 °C, H_2 (4 atm). [f] Isolated yields. [g] Yields determined by NMR spectroscopy. [h] Yields determined by GC analysis.



Scheme 3. Complexes $(PN_{3-5}P)Co^{II}(Cl)_2$ **11a–c** and **12a–c** synthesised by Kempe and co-workers for the hydrogenation of aldehydes and ketones.

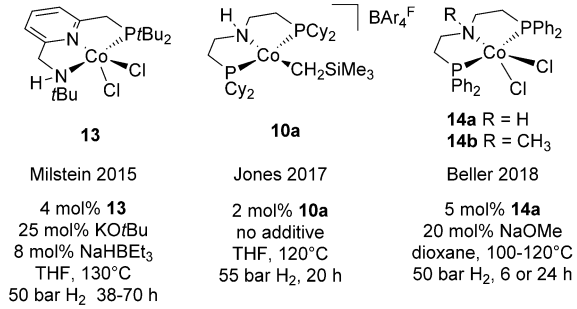
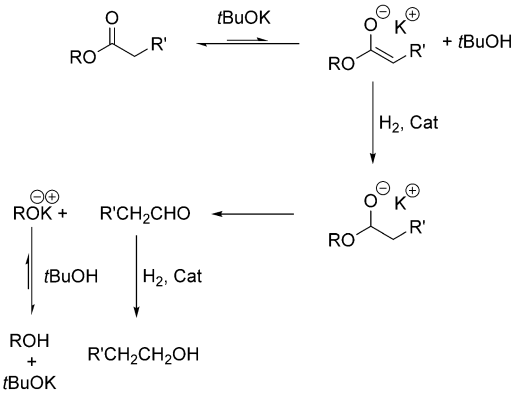


Figure 3. Cobalt–pincer complexes applied in ester hydrogenation.



Scheme 4. Plausible mechanism of ester hydrogenation via an ester enolate intermediate.

The first example of a Co-catalysed ester reduction was reported by Milstein and co-workers using **13**.[34] At relatively high temperature (130 °C) in the presence of 25 mol% of base, the catalyst **13** was able to hydrogenate various primary, secondary and tertiary aliphatic esters in good to high yields. Interestingly, aromatic and fluorinated esters were not reduced. The unexpected catalytic behaviour is explained by the hydrogenation of the enolate, which can be formed from the aliphatic ester and which is in equilibrium with the ester under basic reaction conditions.[35] This mechanism (Scheme 4) has never been reported before for esters hydrogenation, suggesting selectivity for enolisable esters.

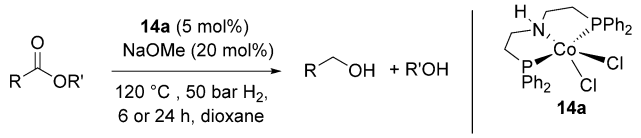
The cationic cobalt–pincer complex **10a** originally developed by Hanson was used by Jones and co-workers for the reduction of esters.[36] Next to slightly improved reaction parameters with respect to **13**, this catalyst reduced aliphatic as well as aromatic esters presenting a wider substrate scope. It is worth pointing out that **10a** works without additives. When **10a** was tested in the hydrogenation of the unsaturated esters methyl and ethyl cinnamate, no selectivity in favour of carbonyl bond reduction was observed. In addition to aliphatic and aromatic esters, also biomass-derived γ-valerolactone was reduced on gram scale with a TON of 3890. Due to the fact that the N-methylated Co pre-catalyst **10c** showed similar catalytic

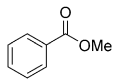
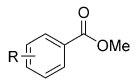
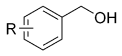
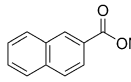
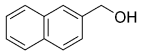
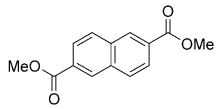
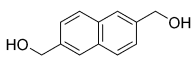
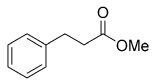
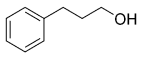
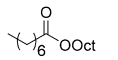
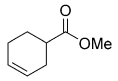
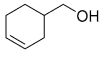
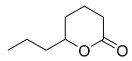
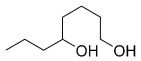
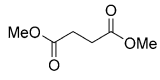
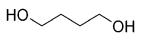
performance in the ester hydrogenation, a classic Schrock–Osborn (inner-sphere)[37] mechanism is postulated instead of MLC.

The most recent example for the hydrogenation of esters mediated by the aliphatic Co–PNP-pincer complex **14a** reported by the group of Beller.[38] The model substrate methyl benzoate was quantitatively reduced to benzylic alcohol at 100 °C, 5 mol% of catalyst loading in only six hours. The substrate scope included several aromatic, aliphatic and cyclic carboxylic acid esters in addition to some biorelevant derivatives such as methyl nicotinate, 2-naphthoate and the related diester (Table 7). Advantageously, this catalytic system also presents selectivity in the hydrogenation of the C=O bond towards the C=C bond. Methyl cyclohex-3-ene-1-carboxylate is reduced to the respective unsaturated alcohol (entry 8). Regarding the mechanism, the pathway discussed by Milstein and co-workers[34] could be excluded for the hydrogenation of aromatic species, since here no formation of an enolate is possible. Furthermore, the complex **14b** bearing a methyl substituent on the nitrogen of the pincer ligand is not active in the hydrogenation of methyl benzoate and methyl octanoate indicating a metal ligand cooperation (MLC).[4] However, DFT computations cannot exclude an inner-sphere mechanism depending on the reaction conditions.

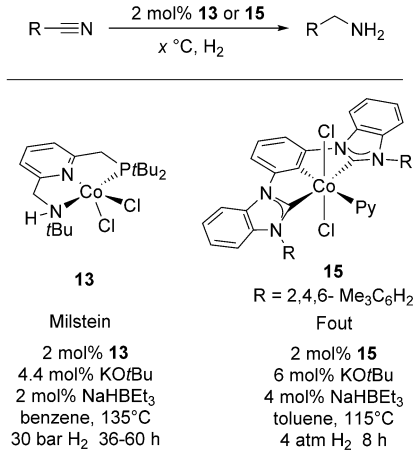
The group of Milstein also described the first homogeneous Co-catalysed hydrogenation of nitriles to primary amines using again the complex (NHNP)Co^{II} **13** (Scheme 5).[39] The challenging part of this reaction is the selective formation of the primary amines avoiding side products. In the optimised system, 2 mol% of **13** were activated with 2 mol% of $NaBHEt_3$ and 4.4 mol% of NaOEt. At moderate conditions (135 °C, 30 atm H_2, 36 h, 2 mL benzene) many (hetero)aromatic nitriles with both electron-donating and electron-withdrawing substituents as well as benzylic and aliphatic nitriles can be hydrogenated to the desired primary amine in good to excellent yield.

Table 7. Selected examples for ester hydrogenation applying cobalt–pincer complex **14a**.[a]



Entry	Ester	Alcohol	Conv. [%][b]	Yield [%][b]
1[c]			>99	99
				
2[c]	R=4-F	R=4-F	99	85
3[c]	R=4-CF_3	R=4-CF_3	99	90
4			99	76
5[d]			95	75
6			99	89
7			63	60
8[c]			79	55
9			90	81[f]
10[d]			92	87

[a] Conditions: substrate (0.5 mmol), **14a** (0.025 mmol), NaOMe (0.1 mmol), dioxane (2 mL), 24 h, 120 °C, 50 bar H_2. [b] Conversion and yield determined by GC analysis using hexadecane as an internal standard. [c] 120 °C, 6 h. [d] **14a** (0.05 mmol), NaOMe (0.2 mmol), 48 h.

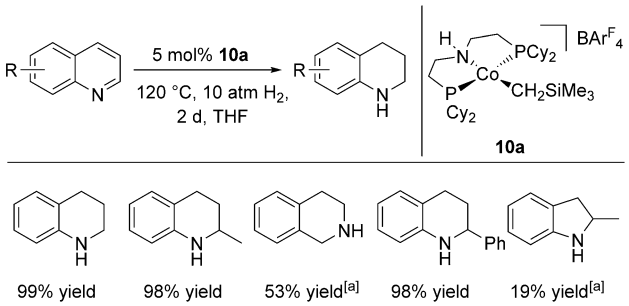


Scheme 5. Co–pincer-based catalyst for the hydrogenation of nitriles.

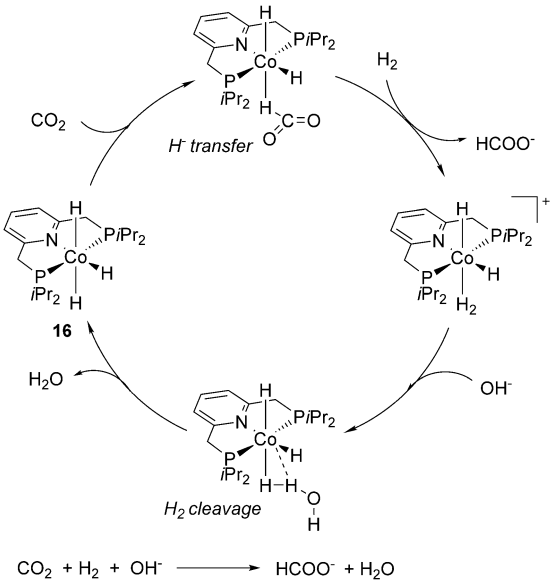
A significant improvement in the nitrile hydrogenation catalysed by Co–pincer complexes has been made by Fout and coworkers, applying the pincer catalyst **15**.[40] This complex can perform the reaction under milder conditions (4 atm H_2, 115 °C, 8 h) compared to the Milstein system, but also in this case an activation with $NaHBEt_3$ is needed. This system provided the hydrogenation of a number of aliphatic and aromatic nitriles in good to excellent yields to the corresponding primary amines. Interestingly, acetonitrile and *tert*-butylnitrile have been hydrogenated for the first time by a first-row homogeneous catalyst. Mechanistic studies revealed the nature of the Lewis acid which facilitates a side-on coordination of the nitriles to the cobalt centre, allowing a transfer of H_2 through a Co$^{I/III}$ redox process.

Inspired by the work of Hanson and their own background on iron–pincer catalysis,[41] the group of Jones applied the isolated Co–PNP system **10a** for the acceptorless, reversible dehy-

drogenation and hydrogenation (see Section 3.1) of N-heterocycles.[42] It is rare that a single transition-metal catalyst is able to realise both reactions, although it is not clear if the active species in these related processes are the same. Notably, almost quantitative conversion was achieved with 5–10 mol% of catalyst **10a**, at 120 °C, 10–20 atm of hydrogen (Scheme 6).



Scheme 6. Hydrogenation of N-heterocycles applying **10a**.



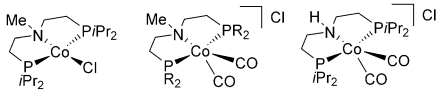
Scheme 7. Mechanism for the formation of formic acid from CO_2 and H_2 catalysed by cobalt–PNP-pincer complex **16**.

The role of the metal ligand cooperativity has been proven by experiments and DFT calculations. While the N-methylated Co complex **10c** completely inhibited the dehydrogenation of 1,2,3,4-tetrahydroquinaldine, the hydrogenation of quinaldine proceeded smoothly to the desired product. These findings suggest that cobalt catalyst **10a** acts in a cooperative fashion in the dehydrogenation part. In contrast for the mechanism of the hydrogenation reaction no involvement of the NH moiety is postulated.

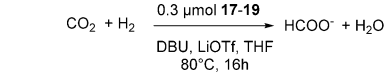
In the last decade, significant improvements have been achieved in the hydrogenation of carbon dioxide to formates as C1 building block for the production of chemicals and fuels. In this regard, many efforts focused on the design of iron and cobalt catalysts showing TON's in the same range as noble-metal-based catalysts. Already in 2011, Yang studied the mechanism for the formation of formic acid from H_2 and CO_2 applying an aromatic PNP-ligated (PNP = 2,6-bis(diisopropylphosphinomethyl)pyridine) cobalt–pincer complex **16** using DFT calculations (Scheme 7).[43] Here, it was found that the reaction pathway with a direct H_2 cleavage by OH^- without the participation of the PNP ligand is about 20 kcal mol^{-1} more favourable than a H_2 cleavage mechanism involving aromatisation/dearomatisation of the pyridine ring in the PNP ligand.

The most important contributions regarding the application of Co–pincer complexes for the reduction of CO_2 was made by Bernskoetter's group.[44] They reported a small family of cobalt pre-catalysts **17**–**19** for CO_2-to-formate hydrogenation and established the important role of Lewis acids as co-catalysts in this reaction (Table 8). Testing these complexes in the CO_2 hydrogenation reaction with the cationic dicarbonyl cobalt complex **18a** a TON of 29000 was achieved in the presence lithium triflate and DBU (entry 4). The catalytic performance of the cyclohexyl-substituted Co–pincer species **18b** showed only a slightly reduced TON indicating the limited influence of the steric effect on the P donor of the pincer ligand (entry 5). Interestingly, the cationic Co–PNP-pincer complex with the NH moiety **19** afforded a lower TON of 450 for the hydrogenation of CO_2 under optimised conditions (entry 6), demonstrating that bifunctional ligand is not advantageous for this type of Co–pincer catalysts.

Table 8. CO_2-to-formate hydrogenation using Co-catalysts **17**–**19**.[a]



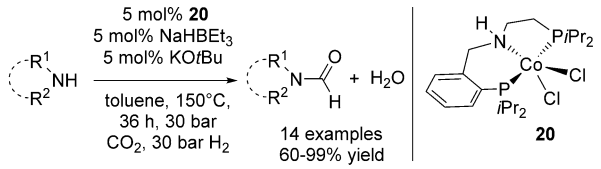
17 **18a** R = *i*Pr, **18b** R = Cy **19**



Entry	Catalyst	TON[c]	Conv.
1	**17**	670	0.8
2	**18a**	10000	13
3	**18a**/no LiOTf	460	0.6
4[b]	**18a**	29000	
5[b]	**18b**	24000	
6[b]	**19**	450	–

[a] Conditions: 1000 psi (69 bar) of CO_2/H_2 (1:1), 0.3 μmol of catalyst, 24 mmol DBU, 4.8 mmol LiOTf in 5 mL THF. [b] CO_2, 500 psi (34.4 bar) H_2 0.3 μmol catalyst, 24 mmol DBU, 3.2 mmol LiOTf in 5 mL MeCN, 45 °C, 16 h. [c] Average TON for three or more trials.

An elegant method for the catalytic application of CO_2 as C1 building block was reported by Milstein and co-workers.[45] They developed a direct N-formylation of amines catalysed by the Co–PNP-pincer catalyst **20** applying CO_2 and H_2 as formylating agent (Scheme 8). A selection of primary and secondary amines was smoothly transferred to the corresponding formamides with 5 mol% **20**, at 150 °C in 36 hours.

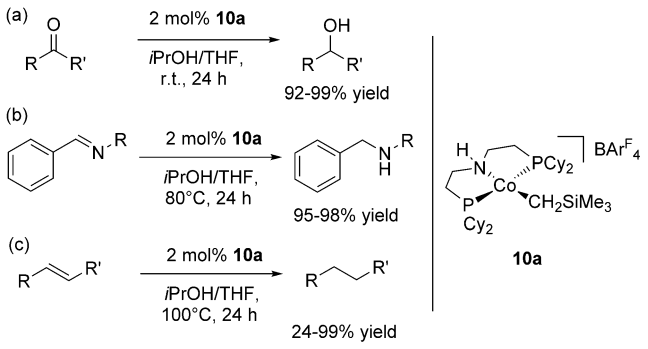


Scheme 8. N-Formylation of amines using CO_2 and H_2 by Co–PNP-pincer complex **20**.

2.2 Catalytic transfer hydrogenation

The catalytic transfer hydrogenation offers a convenient alternative to the reduction by molecular hydrogen and does not require any special set-up in laboratory. In addition, they can be performed often under milder reaction conditions, which can be beneficial with respect to chemoselectivity. Until now, the catalytic applications of Co–pincer complexes for transfer hydrogenation have been scarcely studied.

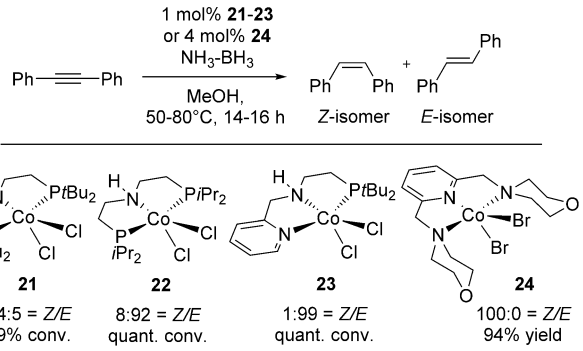
In 2013, Hanson and Zhang published the first study for a cobalt–pincer complex catalysed transfer hydrogenation of C=O and C=N bonds (Scheme 9, reactions a and b).[46] Generating



Scheme 9. Transfer hydrogenation of ketones, aldehydes, imines and olefins by Co–PNP-pincer complex **10a**.

catalyst **10a** in situ from complex **9a** and $H[BAr^F_4]\cdot(Et_2O)_2$, several ketones and aldehydes are smoothly transferred to the respective alcohols with isopropanol as hydrogen source at room temperature. Additionally, some imines reacted to the secondary amines, but here 80 °C was needed. Also, the N-methylated Co–pincer species **10c** displayed similar activity for the transfer hydrogenation of acetophenone as **10a**, showing that metal–ligand cooperativity is not required for this catalysis. This nice work was completed by Zhang demonstrating the catalytic applicability of **10a** for the transfer hydrogenation of substituted terminal and internal olefins under similar conditions (Scheme 9, reaction c).[47]

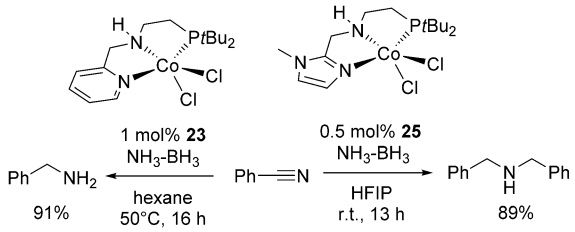
A selective stereo-divergent Co-catalysed transfer hydrogenation of alkynes to *Z*- and *E*-alkenes was developed by Liu and co-workers (Scheme 10).[48] In more detail, they found that the stereocontrol for the semihydrogenation of alkynes strongly depends on the ligand type of the applied Co–pincer catalyst. Using ammonia borane as hydrogen source and the Co–



Scheme 10. Stereoselective transfer semihydrogenation of alkynes by Co–PNP- and Co–NNP-pincer complexes **24**–**24**.

PNP-pincer complex **21** bearing bulky *tert*-butyl substituents preferentially the *Z*-isomers are formed. In order to generate the unusual *E*-isomer, the sequential *Z*-selective alkyne hydrogenation is followed by a *Z*- to *E*-alkene isomerisation.[49] The isomerisation process is promoted by a less steric hindered metal centre, requiring an open coordination site. Thus, a slight change of the PNP-ligand structure from *tert*-butyl to isopropyl substituent of the Co–pincer complex (**22**) resulted in a completely different stereoselectivity yielding mainly the *E*-alkene. The NNP cobalt catalyst **23** with the hemilabile pyridine group produced the *E*-isomer in excellent yield and $>$99:1 *E*/*Z* selectivity. Remarkably, all of these cobalt catalyst pre-cursors **21**–**23** operated under mild conditions and required no additive for the semihydrogenation of various internal and terminal alkynes. Recently, Balamaran and co-workers reported a phosphorous-free Co–NNN-pincer catalyst **24** for this reaction, which worked under similar conditions reducing internal alkynes to the corresponding *Z*-alkene.[50]

A novel approach for the cobalt-catalysed chemodivergent transfer hydrogenation of nitriles was also described by the group of Liu.[51] In the presence of Co–NNP-pincer complexes **23** and **25** and again using ammonia borane as hydrogen donor, nitriles could be reduced to primary or secondary amines depending on the applied solvent (Scheme 11). In



Scheme 11. Stereoselective transfer hydrogenation of nitriles by Co–NNP-pincer complexes **23** and **25**.

hexane the model compound benzonitrile was transferred to benzylamine with 1 mol% of Co–pincer complex **23**, while dibenzylamine is obtained with catalyst **25** in hexafluoroisopropanol (HFIP). The general applicability of this method is proved for the hydrogenation of more than 70 nitriles, including of

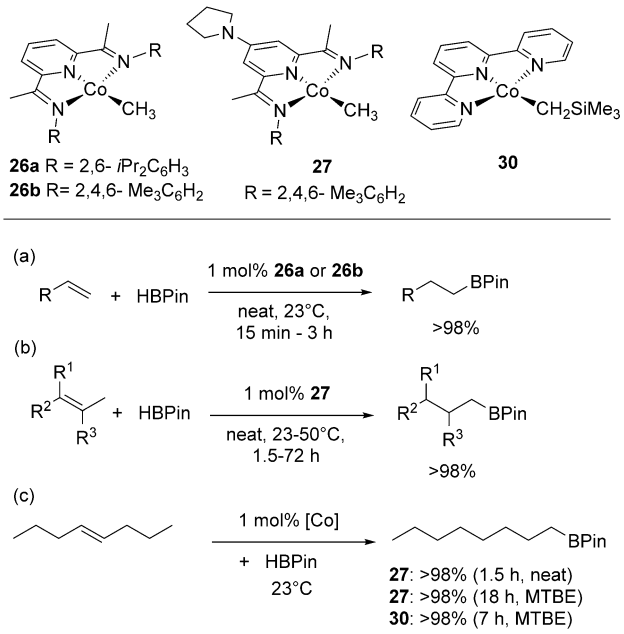
(hetero)aromatic and aliphatic nitriles as well as industrial relevant dinitriles. Mechanistic studies revealed an inner sphere mechanism without the metal–ligand cooperativity.

2.3 Catalytic hydroboration/hydrosilylation

Further hydrogen donors such as hydroboranes and hydrosilanes offer the possibility to reduce unsaturated compounds next to molecular hydrogen or transfer hydrogen reagents. Advantageously, both reaction types (hydroborations as well as hydrosilylations) require milder reaction conditions allowing higher chemoselectivity and improved tolerance of functional groups. Although, they are more expensive and generate unwanted waste, the installation of a B or Si atom can be beneficial regarding subsequent functionalisation (coupling, oxidation, etc.).

2.3.1 Catalytic hydroboration

The first catalytic hydroboration of sterically hindered, non-activated terminal olefins using cobalt–pincer complexes was described by Chirik.[52] When 1 mol% of bis(imino)pyridine cobalt methyl complexes **26a** or **26b** were employed in a neat, equimolar mixture of alkene and pinacolborane (HBPin) at 23 °C the corresponding alkylboronic esters are already formed in 15 min with high anti-Markovnikov selectivity (Scheme 12, reaction a). With more hindered tri- and tetra-substituted internal olefins a cobalt-catalysed tandem isomerisation–hydroboration sequence was observed, in which the boron fragment was placed exclusively at the terminus of the alkyl chain (Scheme 12, reaction b).



Scheme 12. a) Catalytic hydroboration of terminal olefins with HBPin in presence of **26a** or **26b**, b) catalytic hydroboration of internal olefins with **27**, and c) isomerisation-hydroboration of *trans*-4-octene with **27** and **30**.

Therefore, the 4-pyrrolidinyl-substituted bis(imino)pyridine cobalt methyl complex **27** was developed, to establish a more active catalyst by the introduction of an electron-rich substituent in 4-position of the pyridine ligand backbone. Indeed, applying 1 mol% of **27** the isomerisation–hydroboration of *trans*-4-octene was completed after 1.5 hours at 23 °C (Scheme 12, reaction c).

After this influential work of Chirik, various other systems have been published utilising cobalt NNN, PNN, CCC pincer complexes for the hydroboration of alkenes (Figure 4 and Table 9). Huang and co-workers developed a remarkably efficient Co–PNN-pincer complex **28** for the anti-Markovnikov hydroboration of vinylarenes (Table 9, entry 3) and aliphatic α-

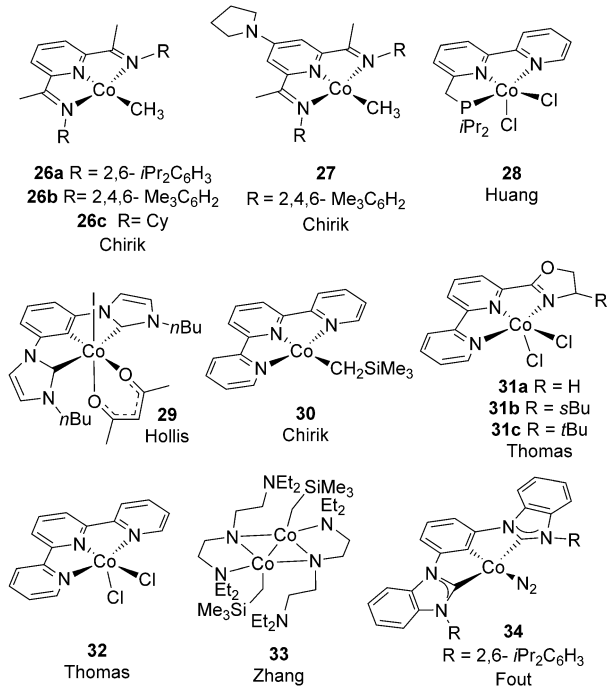
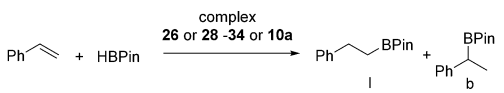


Figure 4. Cobalt–pincer catalysts for the hydroboration of alkenes.

Table 9. Comparison of cobalt complexes for the hydroboration of styrene with pinacolborane.[a]



Entry	Complex [mol%]	Additive [mol%]	Solvent	*T* [°C]	*t* [min]	Yield [%] (l:b)
1[52]	**26a** [1]	–	neat	23	15	>98 (100:0)
2[52]	**26b** [1]	–	neat	23	15	>98 (100:0)
3[53]	**28** [0.05]	$NaBHEt_3$ [2]	THF	25	3	>99 (100:0)
4[54]	**29** [0.3]	$LiBHEt_3$ [1]	THF	22	60	>99 (1:20)
5[55]	**30** [1]	–	MTBE	23	20	>98 (1:25)
6[56]	**31c** [1]	NaO*t*Bu [2]	THF	r.t.	60	>95 (3:97)
7[56]	**32** [1]	NaO*t*Bu [2]	THF	r.t.	60	69 (9:91)
8[57]	**10a** [1]	–	Et_2O	25	60	>99 (92:8)
9[57]	**33** [0.5]	–	Et_2O	25	240	99 (5:95)
10[59]	**34** [2.5]	–	benzene	r.t.	60	88 (100:0)

olefins with HBPin.[53] Most reactions proceeded to completion with 0.005–0.05 mol% of **28** with or without solvent upon activation with $NaBHEt_3$. In a larger scale experiment the hydroboration of styrene (50 mmol) with HBPin was realised with a very low catalyst loading of **28** (0.005 mol%) providing an excellent turnover number (TON) of 19800.

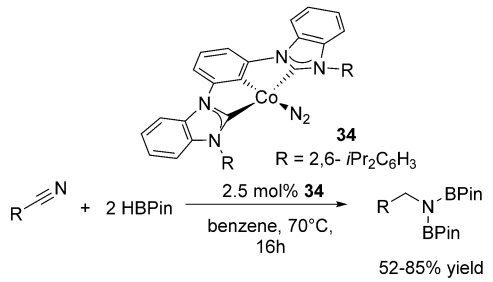
Interestingly, the air-stable Co–CCC-NHC-pincer complex **29**[54] and the cobalt–alkyl-NNN-pincer complex **30**[55] bearing the 2,2′:6′,2″-terpyridine ligand hydroborate styrene favouring the Markovnikov regiochemistry (Table 9, entries 4 and 5) instead of the usual anti-Markovnikov product. When the bipyridyl–oxazoline cobalt complex **31c** was applied for the hydroboration of different substituted styrene derivatives the Markovnikov selectivity could be significantly improved.[56] Thus, the hydroboration of styrene with pinacolborane proceeded with excellent yields and high selectivity for the Markovnikov regioisomer (entry 6). With the terpyridine cobalt complex **32** a moderate yield and a good Markovnikov selectivity for styrene was obtained (entry 7).

While the ionic Co–PNP-pincer complex **10a** quantitatively hydroborated styrene mainly to the linear boronic ester (Table 9, entry 8), with the neutral dinuclear Co–NNN complex **33** again the Markovnikov derivative was formed as major product (entry 9).[57]

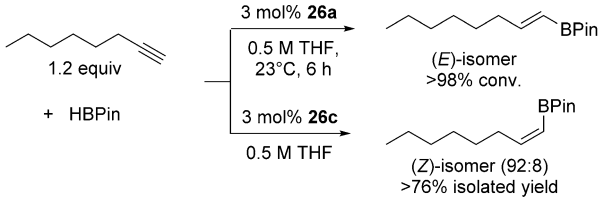
Later, Thomas and co-workers investigated the catalytic behaviour of various known cobalt catalyst systems **26b**, **28** and **5a** in combination with NaO*t*Bu as activator for hydroboration reactions of alkenes and found equal or slightly improved product yields under the applied reaction conditions.[58] This beneficial effect of NaO*t*Bu was explained by the formation of a hypervalent "ate" species from the alkoxide and pinacolborane which serves as hydride donor and allows the generation of a metal hydride complex.

The group of Fout developed the electron-rich, low-valent Co^{I} CCC pincer catalyst **34**, which is active for the hydroboration of alkenes and nitriles.[59] In case of terminal alkenes such as styrene the anti-Markovnikov product was formed (Table 8, entry 10). When the hydroboration of aliphatic, aromatic and heterocyclic nitriles was explored with the Co^{I} CCC pincer catalyst **34**, simple heating of a mixture of 2.5 mol% **34**, pinacolborane and nitriles at 70 °C afforded the bis(borylated)amines in good yields (Scheme 13).

Chirik and co-workers explored the selective anti-Markovnikov hydroboration of terminal alkynes and demonstrated that the modification of the ligand substituent or the reaction parameters allowed for manipulation of the stereochemical outcome of the reaction (Scheme 14).[60] When the hydroboration of 1-octyne and HBPin is conducted with **26a** at 23 °C for 6 h



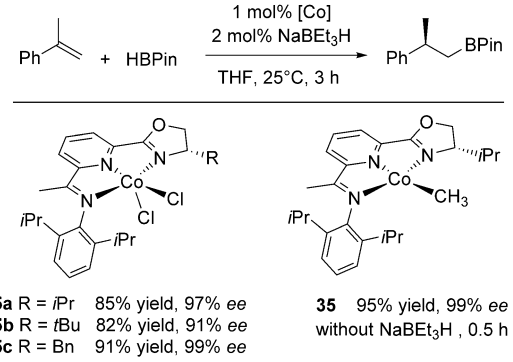
Scheme 13. Hydroboration of nitriles with Co–CCC-pincer complex **34**.



Scheme 14. Hydroboration of 1-octyne with **26a** and **26c**.

in THF the (*E*)-vinylboronate ester is formed in 98% conversion. Realising the catalytic hydroboration reaction with bis(imino)-pyridine cobalt methyl complex **26c**, bearing a cyclohexyl moiety instead of the 2,6-diisopropylphenyl group, the major stereoisomer was (*Z*)-vinylboronate ester with 76% isolated yield. Isotopic labelling and stoichiometric experiments were done to gain insight into the origin of (*Z*)-selectivity. Here, the formation of a metal vinylidene intermediate leading to the *E*-isomer could be excluded.

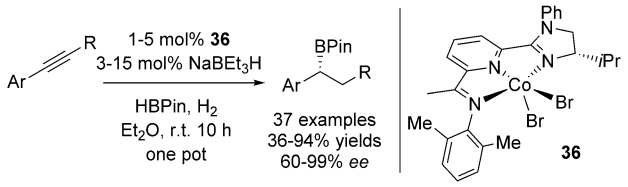
The first enantioselective hydroboration of 1,1-disubstituted alkenes catalysed by a cobalt complex with iminopyridine-oxazoline ligands was reported by the Huang group (Scheme 15).[61] Upon activation with $NaBEt_3H$ the Co dichloride



Scheme 15. Cobalt-catalysed asymmetric hydroboration of α-methylstyrene.

complexes **5a–c** form the alkylboronate ester of α-methylstyrene with HBPin in high yields in up to 99% *ee*. When the Co methyl complex **35** was employed the best result (99% *ee*) was obtained with lower catalyst loading (0.5 mol%) and in shorter reaction time (0.5 h), while no activation was needed.

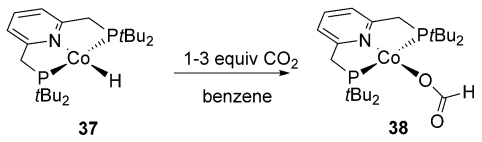
A regio- and enantioselective sequential hydroboration/hydrogenation of internal alkynes with HBPin and H_2 balloon was developed by Lu and co-workers.[62] When the Co–pincer complex **36** coordinated by the more electron rich *N*-phenyl-protected chiral imidazoline-iminopyridine ligand was used a promising yield (85%) and enantioselectivity (97% *ee*) was obtained for the model alkyne (Scheme 16).



Scheme 16. Cobalt-catalysed asymmetric hydroboration/hydrogenation of internal alkynes.

2.3.2 Catalytic hydrosilylation

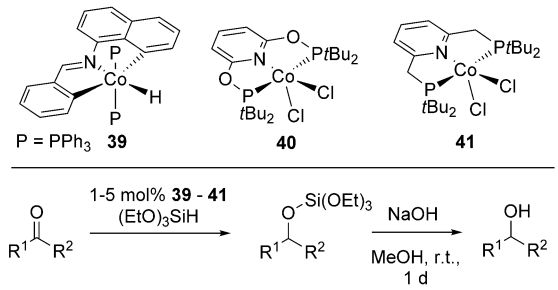
Chirik et al. explored the addition of CO_2 to [(PNP)CoH] **37** resulting in a rapid insertion into the Co–H bond forming **38** (Scheme 17).[63] Furthermore, they found that formate is easily



Scheme 17. Insertion of CO_2 into the Co–H bond of complex **37**.

removed from the Co coordination sphere with $PhSiH_3$, indicating **37** as a suitable pre-catalyst for the hydrosilylation of CO_2. Thus, in the presence of 0.5 mol% of **37** and four equivalents phenylsilane a complete consumption of CO_2 gas was observed in 2 h leading to a mixture of oligomers containing silyl formate (68%), bis(silyl)acetyls (27%) and silyl ethers (9%).

Inspired by the previous work of Chirik, the group of Li synthesised the hydridocobalt(III) complex **39**, bearing a CNC-pincer ligand and studied its catalytic activity for the hydrosilylation of other carbonyl compounds such as aldehydes and ketones (Scheme 18).[64] Here, it was found that complex **39** acted as an efficient catalyst in the presence of triethoxysilane for the reduction of various substituted aldehydes and ketones. When, Findlander and co-workers tested the Co–

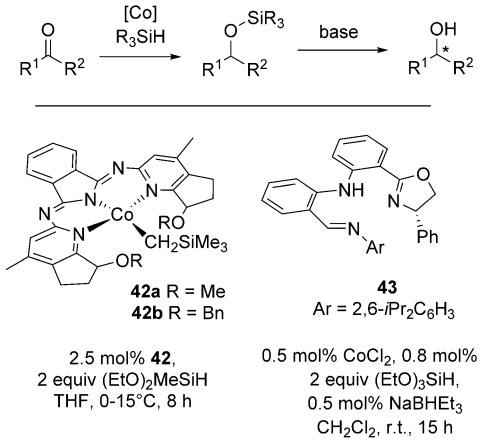


[a] Reaction conditions for **39**: 1-5 mol% **39**, 1 mmol substrate, 1.2 mmol $(EtO)_3SiH$, 2 mL THF, 3-24 h, 60°C.
[b] Reaction conditions for **40** and **41**: 1 mol% **40** or **41**, 1.3 mmol substrate, 1.3 mmol $(EtO)_3SiH$, 2 mol% $NaBHEt_3$, neat, r.t., 24 h.

Scheme 18. Hydrosilylation of carbonyl compounds with Co–pincer complexes **39** to **41**.

PONOP- and Co–PNP-pincer dihalide complexes **40** and **41** in the hydrosilylation of carbonyl compounds the corresponding alcohols were produced in moderate to good yields after activation with two equivalents of $NaBHEt_3$. Notably, also the catalyst systems generated in situ from $CoCl_2$, pincer ligand, $(EtO)_3SiH$ and $NaBHEt_3$ was active in the reduction of aldehydes and ketones.[65]

Also the enantioselective hydrosilylation of ketones with chiral Co–pincer-based catalysts has been explored (Scheme 19). Already in 2012, Gade and co-workers presented

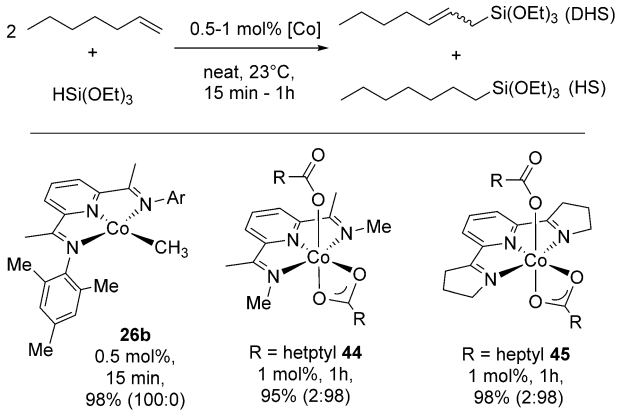


Scheme 19. Co–pincer complexes **42** or $CoCl_2$/**43** for the enantioselective hydrosilylation of ketones.

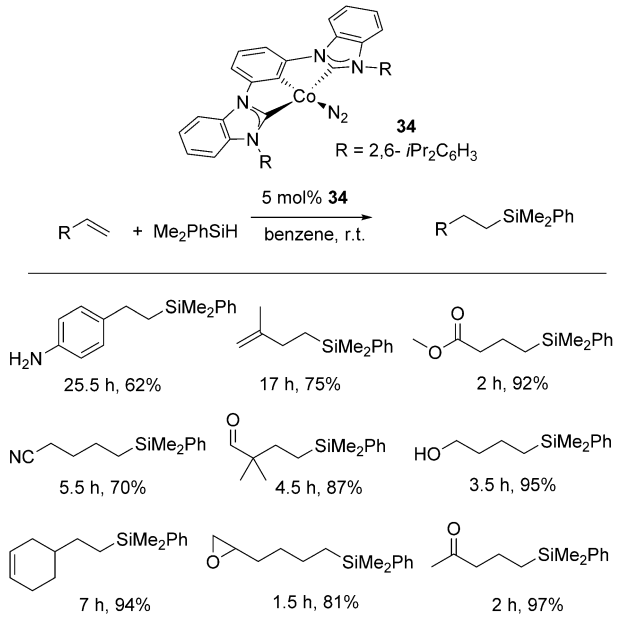
a family of Co–NNN-pincer complexes **42** derived from 1,3-bis(2-pyridylimino)isoindoline framework that facilitated the transfer of prochiral aryl alkyl ketones with high yield and enantioselectivities up to 91% *ee*.[66] An in situ catalyst system composed of $CoCl_2$ and the chiral iminophenyl oxazolinylphenylamine pincer ligand **43** was reported by Chen and Lu. With a catalyst loading of only 0.5 mol% ketones were reduced to the respective chiral alcohols with high enantioselectivities up to 99% *ee*.[67]

Again the Chirik group demonstrated that a rational catalyst design allows to control the selectivity of a given reaction (Scheme 20).[68] While the aryl-substituted bis(imino)pyridine cobalt methyl complex **26b** promoted the catalytic dehydrogenative silylation (DHS) of linear α-olefins to the corresponding allylsilanes (DHS/HS = 100:0),[68a] the N-methyl-substituted and the cyclic bis(imino)pyridine cobalt complexes **44** and **45** resulted in high hydrosilylation (HS) selectivity (> 98%) affording 95–98% product yields.[68b] Here, the coordination of the carboxylate ligand to the cobalt centre in **44** and **45** improved the bench stability of complexes with undiminished high activity.

The well-defined bis(carbene) Co^{I} complex **34** for the efficient, catalytic hydrosilylation of terminal alkenes was presented by Fout and co-workers. The reaction occurred with anti-Markovnikov orientation featuring a broad substrate scope. Alkenes containing hydroxyl, amino, ester, ketone, formyl or nitrile groups were selectively hydrosilylated (Scheme 21).[69]

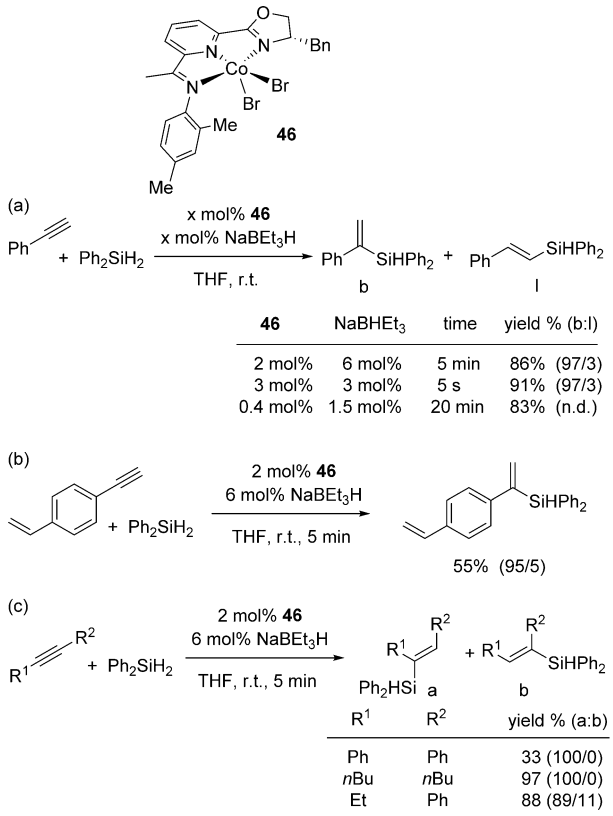


Scheme 20. Dehydrogenative silylation and hydrosilylation of 1-octene.



Scheme 21. Hydrosilylation of terminal alkenes with Co–pincer complex **34**.

A highly chemo-, regio- and stereoselective hydrosilylation of terminal and internal alkynes to α-vinyl silanes was shown by Lu (Scheme 22).[70] For this reaction the Co–pincer catalyst **46** was designed bearing a less bulky 2,4-dimethyl aniline substituent on the pincer backbone as well as two bromine ligands. Phenylacetylene was transformed with 2 mol% of **46** and Ph_2SiH_2 in high regioselectivity (97:3) and 86% yield to the respective vinyl silane in only five minutes. Notably, when the reaction is stopped after 5 s, 91% yield of the silylation products are formed using 1 mol% of **46** which corresponds to an excellent TOF = 65 520 h^{-1}. With further reduced catalyst loading (0.4 mol%) the reaction is finished in 20 minutes affording still 83% yield. 4-Vinylphenylacetylene could be converted in 55% yield to the alkyne hydrosilylation product, while no hydrosilylation of the terminal alkene moiety was observed. Finally, the Co–pincer catalyst **46** is also active in the hydrosilylation of symmetrical aromatic and aliphatic internal alkynes providing only *syn*-addition products. For unsymmetric internal aryl



Scheme 22. Hydrosilylation of terminal and internal alkynes with Co–pincer complex **46**.

alkyl alkynes the 1-aryl-1-silyl-2-alkyl-derivative is available as major product.

3. Catalytic Dehydrogenation Reactions

In general, the removal of H_2 from organic compounds is thermodynamically unfavoured, which is why sacrificial hydrogen donors or stoichiometric amounts of oxidants can be used to facilitate this reaction. In order to overcome these disadvantages, the acceptorless dehydrogenation has been studied intensively in the past decade leading to a number of appropriate catalysts.[71] Here, we summarise the application of cobalt–pincer compounds for acceptorless dehydrogenation reactions including dehydrogenative coupling reactions.

3.1 Acceptorless dehydrogenation

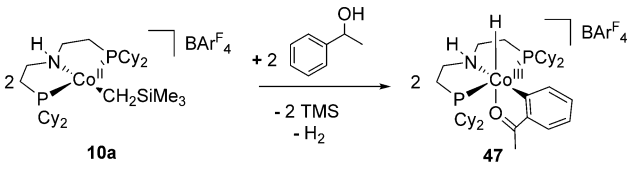
Acceptorless dehydrogenation is a straightforward and effective way to convert amines, imines, alkanes, alcohols, formic acid, and so forth, into the corresponding dehydrogenated products. This method represents an atom-economic and environmentally benign route to synthesise ketones, aldehydes, esters, lactones, alkenes, and alkynes, respectively.

3.1.1 Alcohol dehydrogenation

The acceptorless dehydrogenation of alcohols applying the Co^{II} complex **10a** has been described by Zhang and Hanson

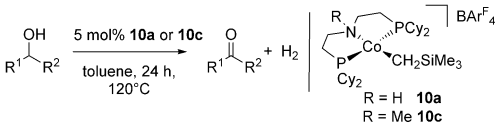
(Table 10).[72] The cationic cobalt(II) alkyl complex **10a** which was generated in situ from the neutral complex **9a** and $H[BAr^F_4]\cdot(Et_2O)_2$ catalyses the dehydrogenation of secondary benzylic alcohols including tetrahydro-1-naphthol and diphenylmethanol to the corresponding ketones within 24 hours in isolated yields between 65–95% (entries 1, 3–8). In case of secondary aliphatic alcohols and 4-methoxyphenylmethanol a slightly reduced activity of **10a** was observed forming the respective products in low to moderate yields (entries 9–11).

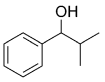
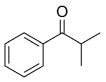
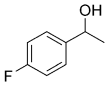
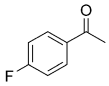
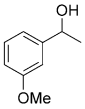
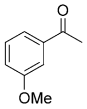
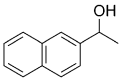
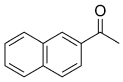
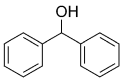
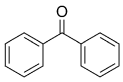
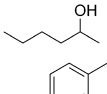
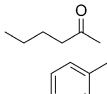
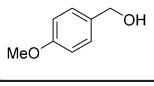
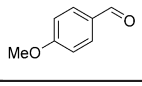
Mechanistic investigations for cobalt-catalysed hydrogenation and dehydrogenation reactions were performed by the same group.[14] Here, the dehydrogenation reaction of 1-phenylethanol using 10 mol% of **10a** was monitored by NMR spectroscopy leading to the detection of a diamagnetic cobalt intermediate with a coordinated acetophenone molecule. Remarkably, the authors also synthesised and isolated this cobalt (acetylphenyl)hydride complex **47** (Scheme 23).



Scheme 23. Proposed balanced reaction for the formation of Co^{III}–PNP-pincer complex **47**.

Table 10. Acceptorless dehydrogenation of selected alcohols using Co-catalysts **10a** and **10c**.[a]



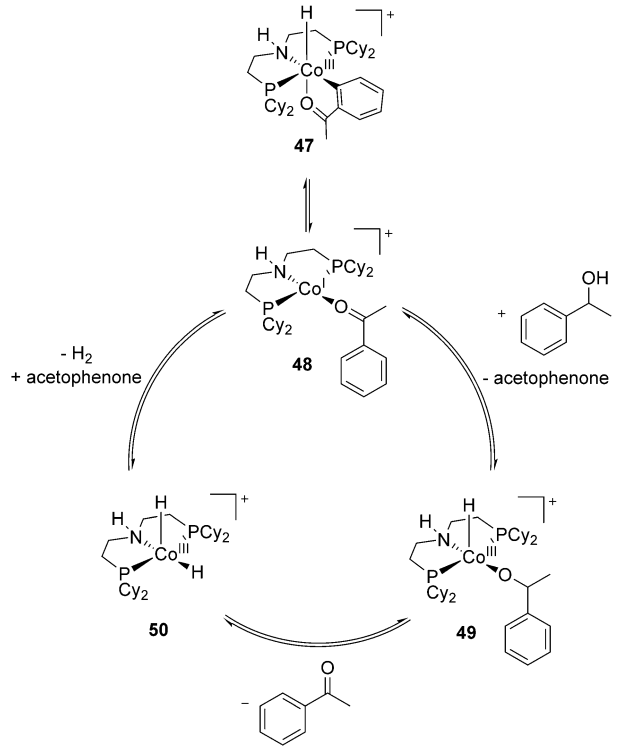
Entry	Alcohol	Product	Yield [%][e]
1			90
2[b]			95
3			81
4[c]			65
5			95
6			92
7			70
8			94
9			56[f]
10[c,d]			64[f]
11			24

[a] Conditions: Substrate (0.5 mmol), 5 mol% catalyst **10a** (5 mol% complex **9a** and 5 mol% $H[BAr^F_4]\cdot(Et_2O)_2$) in toluene (2 mL) in a 100 mL reaction vessel, 120 °C. [b] Substrate (0.5 mmol), 5 mol% catalyst **10c** in toluene (2 mL) in a 100 mL reaction vessel, 120 °C. [c] 42 h. [d] Reaction runs in THF. [e] Isolated yield. [f] Determined by GC.

The unexpected formation of the cobalt(III) species was explained by the following possible pathway: Initially, Co^{II} complex **10a** is reduced to Co^{I} complex by the alcohol 1-phenylethanol, generating acetophenone and TMS. Then, the overall stoichiometry would be balanced by the dehydration of a second molecule of 1-phenylethanol by the Co^{I} species affording again acetophenone and hydrogen. The cobalt(III) (acetylphenyl)hydride complex **47** is generated by the following oxidative addition of the C–H bond from the aromatic ring of acetophenone. Hanson and co-workers confirmed that the hydride ligand in Co complex **47** resulted from the activation of the C–H bond of acetophenone by deuterium-labelling experiments. Interestingly, also the isolated Co^{III} compound **47** is active in the alcohol dehydrogenation (94% yield of acetophenone) indicating that **47** can be regarded as a catalyst resting state.

Notably, the alcohol dehydrogenation of 1-phenylethanol using 5 mol% of the cationic N-methylated Co^{II} complex **10c** yielded 95% of acetophenone demonstrating that the N–H group on the pincer ligand is not mandatory for this reaction (Table 10, entry 2). In summary of the above results, a mechanism for the alcohol dehydrogenation was proposed proceeding through a Co^{I}/Co^{III} cycle (Scheme 24). Starting from **47** a Co^{I} intermediate **48** is formed by reductive elimination of acetophenone allowing a ligand exchange at the cobalt centre by means of associative or dissociative substitution. The oxidative addition of the O–H bond of 1-phenylethanol (or a deprotonation of the alcohol and protonation of the metal complex) generates the corresponding Co^{III} alkoxide complex **49**, which undergoes β-hydride elimination to produce a Co^{III} dihydride species **50**. In the last step, the catalytic cycle is completed by the loss of hydrogen and the coordination of acetophenone or 1-phenylethanol, respectively. The reversibility of the overall reaction was demonstrated experimentally excluding metal ligand cooperativity for this cobalt system.

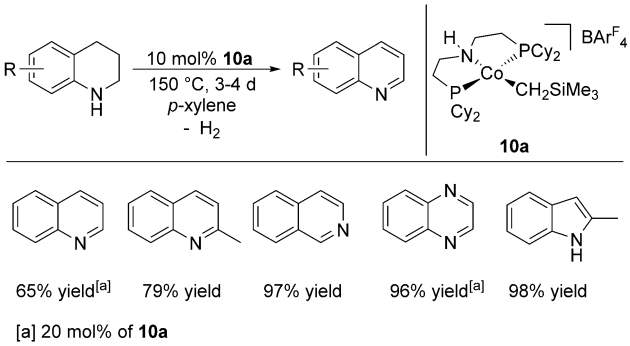
DFT calculations on the mechanism of alcohol dehydrogenation with Co–pincer complexes **10a** and **10c** were carried out by the group of Yang.[31] They computed the lowest relative energy for Co species **47**, as a reason why this compound was observed during the experiments. Furthermore, Yang postulated the oxidative addition of O–H from 1-phenylethanol to Co as the rate-determining step.



Scheme 24. Proposed mechanism of Co-catalysed dehydrogenation of 1-phenylethanol.

3.1.2 C–N bond dehydrogenation

Stimulated by the work above and related iron–pincer catalysis,[41] the group of Jones applied the isolated Co–PNP system **10a** for the acceptorless, reversible dehydrogenation and hydrogenation (see Section 2.1) of N-heterocycles.[42] The de/hydrogenation equilibrium of this thermodynamically non-favoured reaction can be influenced by the remove of H_2 during the reaction.[73] Under optimised conditions (10 mol% **10a**, 150 °C, reflux, 3–4 d), several simple heterocycles, such as 1,2,3,4-tetrahydroquinaldine, six-membered tetrahydroquinoline and five-membered 2-methylindoline were dehydrogenated giving isolated yields between 65–98% (Scheme 25). In addition, catalytic dehydrogenation of 1,2,3,4-tetrahydroquinoxaline containing two amino moieties proceeded smoothly to the desired quinoxaline derivative. When the reactions of



Scheme 25. Dehydrogenation of N-heterocycles.

1,2,3,4-tetrahydroquinoxaline and 1,2,3,4-tetrahydroquinoline were monitored by GC no partially dehydrogenation products were detected indicating that the rate of first amine dehydrogenation step is slower than the second dehydrogenation step. Control experiments proposed isomerisation of the initially formed C=N bond to C=C followed by the second dehydrogenation of the secondary amine moiety.

Interestingly, the respective N-methylated Co complex **10c** was not active in the amine dehydrogenation. Based on this result Jones concluded that the dehydrogenation of N-heterocycles applying Co complex **10a** most likely proceeds in a cooperative fashion involving the N–H moiety of the pincer ligand.

3.1.3 Formic acid dehydrogenation

An important area with respect to hydrogen technology and renewable energy storage is the dehydrogenation of formic acid as a non-toxic liquid with a hydrogen content of 4.4 wt%. Although the CO_2 hydrogenation to formates with cobalt–pincer pre-catalysts is known,[44] no experimental study on the reverse formic acid dehydrogenation reaction has been reported. In 2016, Yang and colleagues proposed a series of cobalt catalysts bearing acylmethylpyridinol and aliphatic PNP-type pincer ligands based on the active site structure of [Fe]-hydrogenase (Figure 5).[74] Based on DFT calculations their potential activity for reversible H_2 storage in the formic acid/CO_2 couple was evaluated. The total free energy barrier was calculated to be as low as 23.1 and 20.9 kcal mol^{-1} in water and THF, respectively, for R^1 = Me, R^2 = OH, and R^3 = NH.

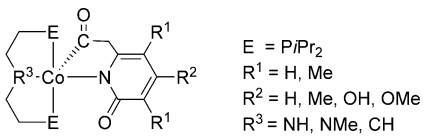


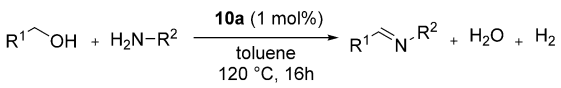
Figure 5. Structure of cobalt-based catalysts computationally designed by Yang and colleagues.

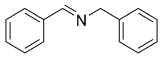
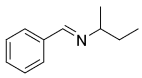
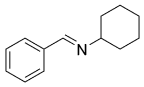
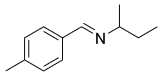
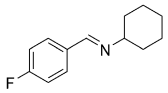
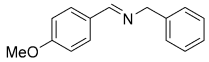
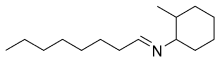
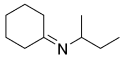
3.2 Dehydrogenative coupling reactions

3.2.1 Dehydrogenative coupling of alcohols with amines

The dehydrogenative coupling of alcohols with amines allows for an atom-economic and waste-avoiding synthesis of imines, amines or amides. The first example of this coupling reaction mediated by a Co–pincer complex was explored by Hanson and Zhang in 2013.[72] Here, various substituted benzyl alcohols reacted with a range of amines as trapping reagents using 1 mol% of in situ generated complex **10a** in refluxing toluene (Table 11). Notably, formation of imines as main product was only observed with the cationic Co species **10a**, while the neutral complex **9a** showed very low conversion after 24 h. For a variety of primary amines high yields of benzylimines as well as aliphatic imines were obtained in 45–52 hours. Also the reaction of the secondary aliphatic cyclohexanol with *sec*-butylamine produced 56% of ketimine (entry 8). No formation of

Table 11. Selected examples for the dehydrogenative coupling of alcohols and amines to imines.[a]



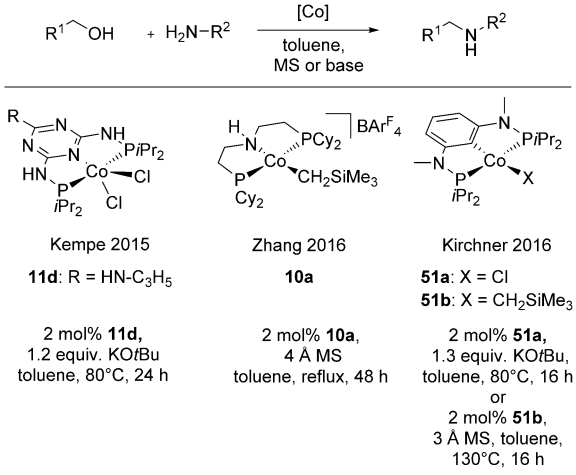
Entry	Product	*t* [h]	GC yield [%][b]
1[c]		27	80 (73)
2		52	96 (85)
3		45	93 (83)
4		50	90 (84)
5		52	74 (61)
6		52	93 (80)
7[d]		50	71
8[d]		48	56

[a] Reaction conditions: 1.0 mmol alcohol, 1.1 mmol amine, 1 mol% catalyst **10a** (1 mol% complex **9a** and 1 mol% $H[BAr^F_4]\cdot(Et_2O)_2$) in toluene (2 mL), 120 °C. [b] Isolated yield in parentheses. [c] 0.2 mol% catalyst **10a**. [d] THF (2 mL).

amides or esters as side products was observed, but in some cases low amounts ($\leq$10%) of the corresponding amine were detected.

The first efficient alkylation of aromatic amines with alcohols catalysed by a cobalt–pincer complex was explored by the group of Kempe in 2015 (Scheme 26).[75] The active Co catalyst **11d** is stabilised by a PN_5P ligand and operates under mild conditions (80 °C) with 2 mol% catalyst loading. A variety of aromatic amines such as aniline, 3-aminopyridine and 1,3-diaminobenzene were selectively monoalkylated with different alcohols in the presence of 1.2 equivalents of KO*t*Bu. Based on this high selectivity, alkylation of diamines with two different alcohols is possible in a two-step procedure leading to unsymmetrically alkylated diamines.

Two additional examples for the cobalt-catalysed N-alkylation of amines with alcohols were reported parallel and independently by the groups of Zhang[76] and Kirchner.[77] Based on the observation that during the imine formation up to 10% of imine are hydrogenated to amine, Zhang and co-workers optimised the reaction conditions by simple addition of molecular sieves (4 Å).[76] Thus, the same cobalt complex **10a** catalysed the selective formation of monoalkylated amines starting from amines and primary alcohols in high yields. Noteworthy, in



Scheme 26. Co–pincer complexes for coupling reactions of alcohols and amines.

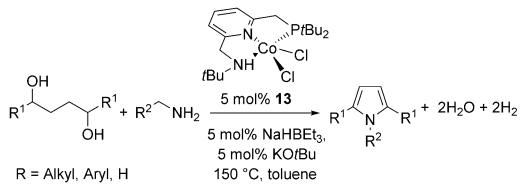
case of the secondary alcohol cyclohexanol a reduced activity and selectivity was found yielding 48% of *N*-cyclohexylaniline as major product.

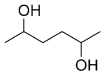
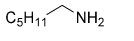
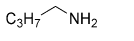
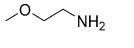
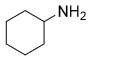
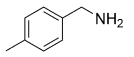
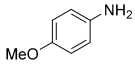
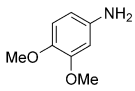
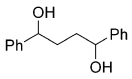
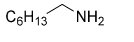
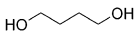
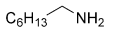
Kirchner established two Co^{II} complexes **51a** and **51b**, which are stabilised by an anionic PCP-pincer ligand based on the 1,3-diaminobenzene scaffold for this N-alkylation reaction.[77] While complex **51a** alkylated aromatic amines with primary alcohols in the presence of 1.3 equivalents of base at low temperature (80 °C), the Co species **51b** bearing the basic ligand CH_2SiMe_3 worked under base-free conditions requiring molecular sieves and 130 °C. In none of these cases tertiary alcohols could be applied for the alkylation of amines, which is in agreement with the assumed hydrogen borrowing mechanism.

Pyrroles can be generated from diols and amines by a dehydrogenative coupling reaction mediated by the cobalt–PNNH-pincer complex **13**, which was developed by Milstein for hydrogenation of carboxylic acid derivatives.[78] Under optimised reaction conditions 2,5-dihydroxyhexane and different amines formed the respective 1,2,5-substituted pyrroles with the extrusion of water and H_2 as the only by-product (Table 12). While linear primary alkyl and benzyl amines provided the products in good-to-excellent yield (entries 1–5, 8 and 9), the reaction of less nucleophilic anilines with 2,5-hexanediol led only to poor yields (entries 6 and 7). Attempts to isolate the active Co^I catalyst or an in situ generated intermediate from the reaction mixture failed. Nevertheless, metal–ligand cooperation (MCL) by amine/amide and aromatisation/dearomatisation ligand transformation was discussed.[79]

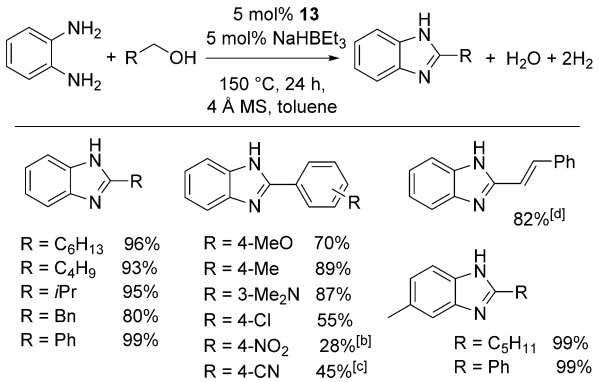
In analogy to their own previous work, Milstein and co-workers investigated also the dehydrogenative coupling of primary alcohols and aromatic diamines which lead to the formation of functionalised 2-substituted benzimidazoles (Scheme 27).[80] Again, the Co–PNNH-pincer complex **13** was the most suitable and active candidate of the tested complexes for this transformation. Under base-free conditions **13** catalysed the synthesis of several benzimidazoles in high yields at 150 °C in the presence of molecular sieves. As possible mechanism, initially Co^I-

Table 12. Selected results for the dehydrogenative coupling of diols and amines using Co complex **13**.[a]



Entry	Diol	Amine	*t* [h]	Yield[b] [%]
1			24	88
2			24	93
3			24	90
4			24	70
5			24	87
6			36	25[c]
7			36	22[c]
8			36	56[c]
9			24	58[c]

[a] Conditions: diol (0.5 mmol), amine (0.5 mmol), 5 mol% catalyst **13**, toluene (2 mL), and 4 Å molecular sieves heated in a closed Schlenk tube for 24–36 h. [b] Yield of isolated product. [c] Yield determined by GC.



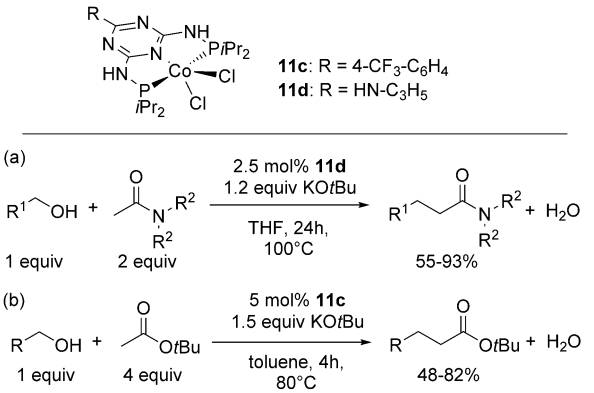
[a] Conditions: diamine (0.5 mmol), primary alcohol (0.5 mmol), 5 mol% catalyst **13**, toluene (2 mL), and 4 Å molecular sieves heated in a closed Schlenk tube for 24h. Yield of isolated product. [b] 2-(4-Aminophenyl) benzimidazol was detected as by-product. [c] KO*t*Bu (5 mmol) was added. [d] 2 equiv crotononitrile were added as hydrogen acceptor.

Scheme 27. Dehydrogenative coupling of 1,2-diaminobenzenes and alcohols catalysed by Co complex **13**.[a]

catalysed dehydrogenation of the primary alcohol to the aldehyde and hydrogen gas is suggested. Subsequently, an imine intermediate is formed by coupling reaction with the diamine eliminating water. In the following cyclisation 2,3-dihydro-1*H*-benzimidazole is formed, which rapidly dehydrogenates to the corresponding benzimidazole derivative.

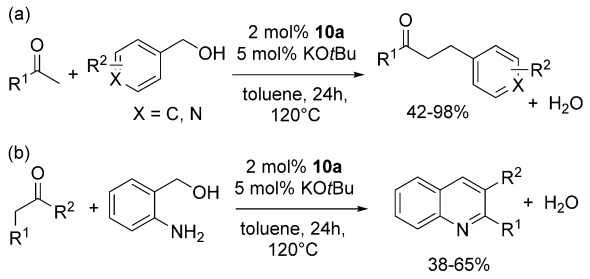
3.2.2 Dehydrogenative coupling of alcohols with carbonyl compounds

An elegant approach to modify amides and esters by α-alkylation with alcohols was developed by Kempe and Deibl applying complexes **11 c** and **11 d** (Scheme 28).[81] Both Co compounds are stabilised by a PN_5P-pincer ligand backbone and act via the borrowing hydrogen concept. The unique feature of this ligand class is activation of complexes by a base leading to double deprotonation of the ligand scaffold and removal of chloride.[33] In general, alkylation of the amides is a challenging reaction due to their low CH acidity. Nevertheless, this transformation worked under relatively moderate conditions using 2.5 mol% of Co compound **11 d** in THF at 100 °C with 1.2 equivalents of KO*t*Bu (Scheme 28 a). In the presence of a twofold excess of amide with respect to alcohol dehydrogenative coupling reaction proceeded smoothly with up to 93% isolated yield. Mechanistic investigations of the α-alkylation of amide indicated that the alcohol oxidation is the rate-limiting step, while the reduction of the C=C double bond of the formed intermediate is comparably fast. α-Alkylation of esters which easily undergo side reactions was realised with 5 mol% of Co pre-catalyst **11 c** in toluene at 80 °C and 1.5 equivalents of KO*t*Bu (Scheme 28 b). The corresponding C-alkylation products were obtained in moderate to good isolated yields when four equivalents of *tert*-butyl acetate are used. A monitoring of the catalytic reaction showed a fast transesterification of *tert*-butyl acetate. The final shift of the equilibrium to the alkylated butyl ester took place by consumption of the primary alcohol.



Scheme 28. Dehydrogenative coupling of a) amides or b) esters with primary alcohols catalysed by **11 c** and **11 d**.

In 2017, Zhang and co-workers adopted the borrowing hydrogen strategy to the α-alkylation of ketones applying Co^{II} complex **10 a** (Scheme 29 a).[82] Here, 2 mol% of **10 a** catalysed

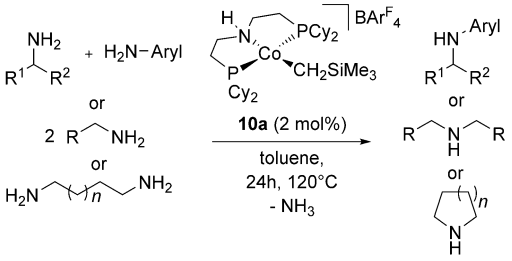


Scheme 29. Dehydrogenative coupling of ketones with a) primary alcohols or b) catalytic Friedländer annulation reaction catalysed by **10a**.

the dehydrogenative coupling of acetophenone with a range of aromatic and aliphatic alcohols as well as of various ketones with benzylic alcohols or pyridylmethanol in the presence of 5 mol% of KO*t*Bu at 120 °C in toluene. Furthermore, Co complex **10a** was established for the one-pot synthesis of quinoline derivatives. For this catalytic version of the Friedländer annulation reaction 2-aminobenzyl alcohol was used as alkylating agent which formed the respective quinolines in up to 65% yield by coupling with ketones (Scheme 29b).

3.2.3 Dehydrogenative coupling of amines with amines

Inspired by the ability of **10a** to dehydrogenate cyclic amines to imines[42] again Zhang and colleagues investigated the selective cobalt-catalysed *N*-alkylation of amines with other amines through the hydrogen borrowing procedure (Scheme 30).[83] The method worked well with 2 mol% catalyst loading (**10a**) at 120 °C in toluene for the synthesis of secondary aromatic, aliphatic and cyclic amines. As in some cases homocoupling of alkyl amines was observed, only one type of amine was used for the *N*-alkylation producing symmetric secondary amines. Finally, the intramolecular alkylation of diamines to cyclic secondary amines proceeded smoothly in up to 91% isolated yield under optimised catalytic conditions.

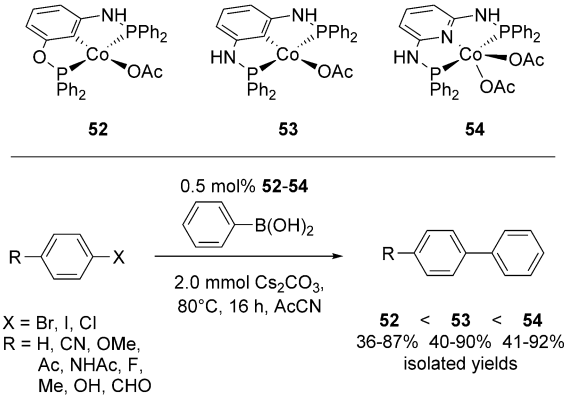


Scheme 30. N-Alkylation of amines with amines catalysed by **10a**.

4. Miscellaneous

4.1 Bond-forming reactions

The first example using Co–pincer complexes for a Suzuki–Miyaura cross coupling reaction was studied by Bhat and coworkers.[84] Therefore, a series of Co PNCOP, PNCNP and PNNNP complexes **52**–**54** was synthesised and examined for the coupling of phenylboronic acid and *p*-substituted aryl halides (Scheme 31). Based on magnetic and spectroscopic measurements for complexes **52** (PNCOP) and **53** (PNCNP) a four-coordinated low-spin, square-planar Co^{II} species was discussed, while in case of **54** (PNNNP) a penta-coordinated Co^{II} compound was expected to be formed.

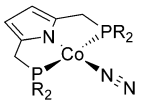


Scheme 31. Suzuki–Miyaura cross coupling of *p*-substituted aryl halides with phenylboronic acid catalysed by **52**–**54**.

All three catalysts showed activity under optimised reaction parameters (acetonitrile, 16 h, 80 °C, 2.0 mmol Cs_2CO_3). The highest catalytic activity was obtained for complex **54** with the PNNNP-pincer ligand, which was explained with an increased electron-donating ability of the ligand by the rising number of N atoms in the ligand backbone.

4.2 Activation of CH bonds or small molecules

Activation of CH bonds or small molecules, such as dinitrogen, continues to attract the interest of numerous scientists because of the fundamental importance for basic science as well as the industrial interest in such transformations. Often, they belong also to the most challenging reactions in chemistry due to the very high bonding energy. As an example, N_2 activation was realised even in a catalytic fashion with Co–pincer complexes, albeit a very strong reductant was needed.[85] More specifically, a direct formation of ammonia from molecular dinitrogen applying the pyrrole-derived PNP-pincer type Co complexes **55a**,**b** was developed by Yoshizawa, Nishibayashi and co-workers (Scheme 32). They designed complexes with an anionic PNP-type pincer ligand **55a**,**b** in which the cobalt centre is stabilised by hard and soft ligand donor groups. In the distorted square-planar Co^{I} species **55a** the dinitrogen ligand is placed in a terminal coordination mode, which was probed by X-ray analysis and IR spectroscopy. Using **55a**, 4.2 equiv of ammonia (based on the catalyst) were obtained at atmospheric pressure of dinitrogen with 40 equiv of KC_8 as a reductant and 38 equiv of $[H(OEt_2)_2]BAr^F{}_4$ as a proton source at −78 °C within 1 hour. The same amount of ammonia is formed in MeO*t*Bu (MTBE) as solvent. The cobalt dinitrogen ligand **55b** was slightly lower active in this reaction. Using $^{15}N_2$ gas the authors confirmed that molecular dinitrogen was converted to



55a R = *t*Bu
55b R = Cy

(a)

N_2 + KC_8 + $[H(OEt_2)_2]BAr^F{}_4$ → (1 eq. **55**; solvent; - 78°C, 1 h) → NH_3 + NH_2NH_2

1 atm 40 equiv 38 equiv

cat.	solvent	NH_3 [equiv][b]	NH_2NH_2 [equiv][b]	Fixed N atoms [equiv][c]
55a	EtO_2	4.2±0.1	0	4.2
55a	MTBE	4.0±0.3	0.1±0.1	4.2
55b	EtO_2	3.1±0.1	0.1±0.1	3.3

[a] **55a** or **55b** (0.01 mmol, 1 equiv), reductant (0.4 mmol, 40 equiv), $[H(OEt_2)_2]BAr^F{}_4$ (0.38 mmol, 38 equiv), 1 atm N_2, 1 h, -78°C. [b] Based on the amount of catalyst. [c] Number of fixed N atoms (equiv) = [NH_3 (equiv)] + 2 [NH_2NH_2 (equiv)].

(b)

N_2 + KC_8 + $[H(OEt_2)_2]BAr^F{}_4$ → (1 equiv **55a**; EtO_2; - 78°C, 1 h) → NH_3 + NH_2NH_2

1 atm 200 equiv 184 equiv

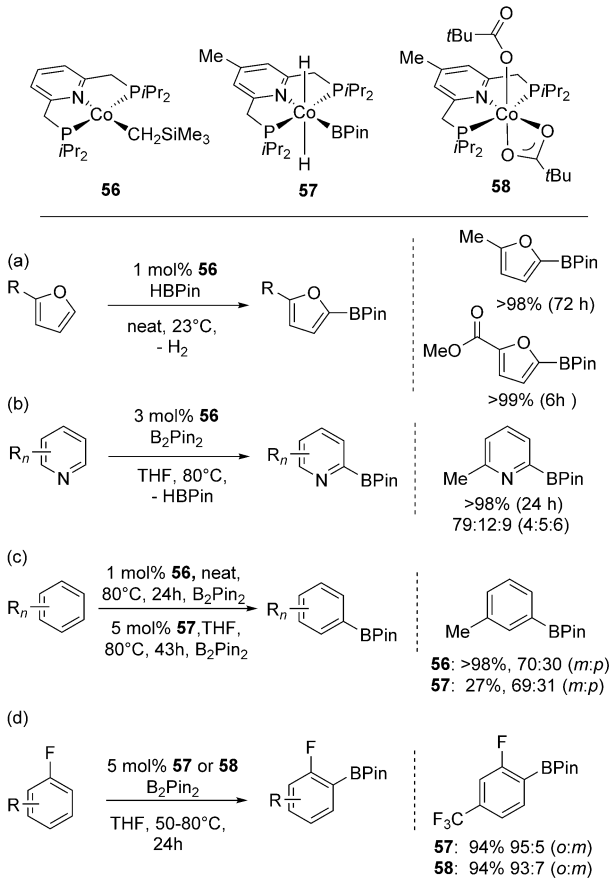
15.9±0.2 equiv of NH_3
1.0±0.4 equiv of NH_2NH_2
17.9 equiv of fixed N atoms

Scheme 32. Catalytic reduction of dinitrogen to ammonia with **55a**,**b** as catalysts.[a]

ammonia. Evidently, such model studies are scientifically interesting, but have no implications for any practical ammonia synthesis.

Furthermore, Co–pincer type complexes have been reported for activation of CH-bonds. Here, the groups of Kirchner and Danopoulos performed stoichiometric reactions and investigated organometallic aspects of this methodology.[86] On the other hand, Chirik and co-workers focused on the catalytic borylation of heterocycles and arenes via C–H functionalisation. For this purpose, they developed the complex **56**, in which the π-acidic imine arm in the ligand backbone is replaced by a σ-donating phosphine in order to create a more electron rich base metal centre.[87] This Co–pincer complex was active for the C(sp2)–H borylation of five-membered heterocycles, pyridines and arenes. 2-Methylfurane and other five-membered heterocycles are exclusively borylated under neat conditions in the position adjacent to the heteroatom (Scheme 33 a). 2,6-Lutidine is selectively functionalised with 3 mol% of **56** in 4-position, 2-substituted pyridines such as 2-methylpyridine underwent smoothly catalytic mono-borylation with a mixture of isomers (Scheme 33 b).

The borylation of simple hydrocarbon arenes was realised in a 20:1 ratio of arene:B_2Pin_2 with 1 mol% of **56** (Scheme 33 c). After 24 h at 80 °C the boron products were detected in 75-98% conversion (based on consumption of B_2Pin_2). For toluene two *meta*- and *para*-products are formed with a selectivity of 70:30. Mechanistic studies supported a Co^I/Co^{III} pathway, in which a cobalt(I)-boryl is responsible for the C–H activation.[88] Substitution of the 4-position of the pyridine moiety in the pincer ligand prevented catalyst deactivation by C–H borylation of the ligand. Based on this observation an improved, second generation of 4-methyl-substituted catalyst **57** and the



Scheme 33. Catalytic C(sp2)–H borylation of five-membered heterocycles, pyridines, and arenes with **56**–**58** as catalysts.

air-stable Co–pincer derivative **58** have been prepared showing high *ortho*-to-fluorine selectivity in the C(sp2)–H borylation of fluorinated arenes (Scheme 33 d).[89]

5. Summary

The development of new pincer-based catalysts, especially derived from non-noble metals such as cobalt, iron or manganese has become a "hot topic" in organometallic chemistry and homogeneous catalysis. In this respect, also homogeneous catalysis with cobalt complexes has been re-invented. After being popular for polymerisations or olefin reductions, cobalt–pincer complexes started a second career as interesting catalysts. In the last decade, several motivating discoveries were made, which we summarised in this review. The diversity in catalysis has been significantly expanded and nowadays they can be considered for all kinds of hydrogenations, dehydrogenations, transfer hydrogenations, as well as hydroborations and hydrosilylations. Although the activity and stability of these systems still needs to be improved this should be possible in the coming years. Notably, often the reactivity of such complexes can be well-explained and this understanding should pave the way for the rational development of more selective and active catalysts. Finally, this might lead to industrial applications of such complexes.

What can we expect from cobalt–pincer complexes in the future or in which direction should this field develop? As shown in this review, an interesting feature of several representatives of this class of complexes is the "non-innocent nature" of the ligand. This involvement of the ligand evidently enlarges the possibilities for specific bond activation by secondary interactions, which can lower the activation barrier of rate determining reaction steps. Notably, most enzymatic and heterogeneous catalysis are facilitated by such secondary interactions, too. Hence, molecular-defined pincer complexes build a bridge towards these fields in catalysis. Due to the multidentate nature of pincer ligands the resulting complexes are often well-defined and stable. Nevertheless, so far their stability and catalyst productivity is still too low for large scale applications. Hence, better understanding of the deactivation pathways of these complexes in catalysis is highly desired.

An important point currently is also the price of most pincer ligands. Clearly, remarkable progress in catalysis has been achieved using inexpensive 3d metals; however, in most cases the ligand is the price-determining part. Thus, the development of "cheap ligands", for example, non-phosphorus-containing systems is also anticipated.

Furthermore, new catalysts will always lead to the discovery of unexpected reactivity. This will induce new catalytic applications, which we do not foresee today. The reader is invited to take an active part in this exciting development!

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Conflict of interest

The authors declare no conflict of interest.

Keywords: (de)hydrogenation · bond formation · homogeneous catalysis · cobalt · pincer complex · transfer hydrogenation

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