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Cobalt pincer complexes for catalytic reduction of nitriles to primary amines†

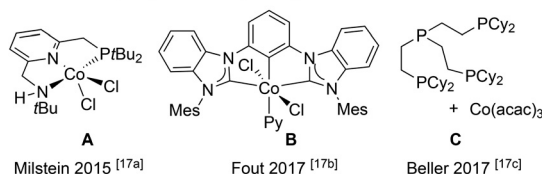
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Various cobalt pincer type complexes **1–6** were applied for the catalytic hydrogenation of nitriles to amines. Among these, catalyst **4** is the most efficient, allowing the reduction of aromatic as well as aliphatic nitriles in moderate to excellent yields.

Hydrogenation of nitriles is applied as a valuable method for the preparation of amines, which represent important target molecules in organic chemistry as well as building blocks in life science industries for pharmaceuticals and agrochemicals.¹ On the laboratory scale, this transformation is often realized with (over) stoichiometric amounts of sensitive organometallic reagents (e.g. LiAlH₄ or NaBH₄) and suffers from poor selectivity and waste generation.² In industry, heterogeneous systems such as RANEY® nickel and RANEY® cobalt are commonly used for the reduction of nitriles but they come along with limited product selectivity or low functional group tolerance.³ Therefore, homogeneous catalytic hydrogenation of nitriles offers a convenient and atom-economic alternative for amine synthesis, operating with higher selectivity and under milder reaction parameters. Compared to the related reduction of imines or nitro compounds,⁴ this reaction is still less explored. So far, mainly traditional catalyst metals such as Rh,⁵ Ru,⁶ Ir,⁷ Re,⁸ or Mo⁹ have been investigated. Due to economic and ecological demands, the replacement of these precious metals by cheaper, more abundant and less toxic 3d metal systems is one of the hot topics in catalysis.¹⁰ In accordance with this actual trend, iron¹¹ and manganese¹² derived catalysts have been developed for the catalytic hydrogenation of nitriles. In addition to this, cobalt complexes offer an inexpensive alternative to precious metal catalysts due to their low cost and availability. Until recently, compared to iron and manganese involving systems, they were much less investigated.¹³ Thereby, cobalt

compounds, and here especially cobalt pincer type complexes¹⁴ show remarkable efficiency in catalytic transformations including polymerization, (transfer) hydrogenation, hydrosilylation/hydroboration as well as N₂ or CH activation.¹³ Although cobalt catalyzed reductions of carbonyl compounds including ketones, aldehydes, or esters¹⁵ and of olefins were intensively studied,¹⁶ only a few homogeneous cobalt catalysts are known for the selective reduction of nitriles to primary amines (Fig. 1).¹⁷ In 2015, the group of Milstein published the first homogeneous Co system for the hydrogenation of nitriles to amines applying the lutidine-based Co pincer complex **A** (Fig. 1).^{17a} This catalyst bearing a PNN^H pincer ligand with a secondary amine side arm allowed potential metal–ligand cooperation (MLC). Although **A** showed an increased catalytic activity compared to its Co PNP and PNN pincer counterparts,^{15a} the reduction of aromatic nitriles required a relatively high temperature (135 °C) and long reaction time (36–60 hours). Fout and co-workers performed the reduction of aromatic and aliphatic nitriles by applying **B** under milder reaction conditions (115 °C; 8 h) but without KO^tBu, and a secondary imine was formed.^{17b}

• Selective hydrogenation to primary amines:



• Hydrogenation to secondary imines:

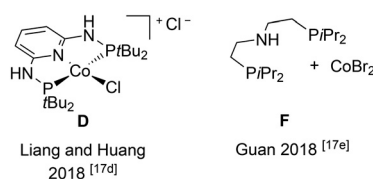


Fig. 1 Cobalt complexes for catalytic hydrogenation of nitriles.

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In addition, a non-pincer based *in situ* combination of $\text{Co}(\text{acac})_3$ and the tetradentate P-donor ligand (tris[2-(dicyclohexylphosphino)ethyl]phosphine) **C** was developed by our group.^{17c} Very recently, the Co PN^3P pincer complex **D**^{17d} and the *in situ* system **F**^{17e} prepared from CoBr_2 and the pincer ligand $\text{NH}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2$ were presented for the cobalt catalyzed hydrogenation of nitriles to the corresponding secondary imines, which normally are only observed as an intermediate within the synthesis of primary amines. Thus, especially regarding the catalyst efficiency and applied reaction parameters, there is still room for improvement.

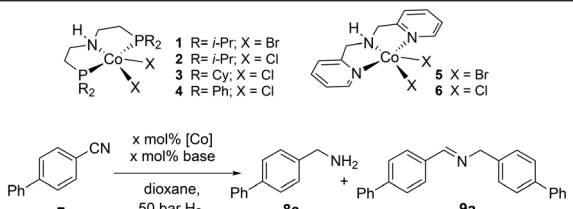
Based on our previous work on non-noble metal catalysis, especially the application of pincer type complexes,^{11a,b,12,15d} we became interested in the development of a defined Co catalyst with aliphatic pincer ligands for the selective hydrogenation of nitriles. At the start of this project, we tested a selection of cobalt pincer complexes bearing different substituents on the phosphorous atom (1–4) as well as two Co complexes with an N_3 donor pincer ligand (5 and 6) (Table 1). The reaction parameters were studied, choosing 4-phenylbenzonitrile (**7a**) as the model compound for the cobalt-catalysed hydrogenation of nitriles. Full conversion to 4-phenylbenzylamine (**8a**) was achieved with 5 mol% of the phenyl substituted Co PNP pincer complex **4** in the presence of 20 mol% NaOMe in dioxane at 140 °C and 50 bar H_2 after 24 h. After full conversion, formation of black particles was observed. Interestingly, up to 40% conversion to the primary amine **8a** and the corresponding intermediate **9a** are found by applying the filtered black precip-

itate in the catalytic test reaction (entry 4). Obviously, the Co PNP pincer complex **4** tends to decompose, forming cobalt nanoparticles which are known to catalyse the nitrile reduction. When catalyst **4** was tested without a base, only small amounts of products **8a** and **9a** were detected, while NaOMe alone did not show any conversion (entries 2 and 3).

In order to prevent the decomposition of the homogeneous cobalt catalyst, the benchmark reaction was performed at lower temperature and shorter time (entries 6–10). At 120 °C, a clear red solution was obtained after a 6 h reaction time and the nitrile was completely transformed into a primary amine. Notably, the time and temperature could be further reduced (80 °C, 4 h) and a quantitative yield of **8a** was obtained with 4 mol% catalyst loading.

The type of base plays a crucial role in the efficiency of the catalyst. With 2 mol% of Co PNP complex **4** and 8 mol% of NaOMe, the catalytic activity dropped down, while in the presence of 8 mol% NaBHET_3 , 98% of 4-phenylbenzylamine (**8a**) was produced (entries 11 and 12). Finally, Co pincer based complexes bearing different substituents are used under these optimized reaction parameters (2 mol% cat., 8 mol% NaBHET_3 , 50 bar H_2 , 80 °C, 4 h, dioxane). Here, Co PNP complexes (1–3) with *i*-propyl and cyclohexyl moieties on the phosphorous atom showed little conversion but no product yield (entries 13–15). Also, two Co complexes with an N_3 pincer ligand (5 and 6) demonstrated moderate catalytic activity producing 4-phenylbenzylamine (**8a**) in 50% yield (entries 16 and 17).

Table 1 Initial screening of reaction parameters and Co pincer catalysts for the catalytic hydrogenation of 4-phenylbenzonitrile (**7a**)^a

					
Entry	Cat. [mol%]	NaOMe [mol%]	<i>T</i> [°C]/ <i>t</i> [h]	Conv. [%]	Yield 8a ^b [%]
1	4 [5]	(20)	140/24	>99	96 (3)
2	4 [5]	—	140/24	26	5 (15)
3	—	(20)	140/24	—	—
4	Iso. np	—	140/24	40	23 (17)
5	Iso. np	—	80/6	—	—
6	4 [5]	(20)	120/18	>99	>99
7	4 [5]	(20)	120/6	>99	>99
8	4 [5]	(20)	100/4	>99	>99
9	4 [5]	(20)	80/4	>99	>99
10	4 [4]	(16)	80/4	>99	>99
11	4 [2]	(8)	80/4	52	3 (44)
12 ^c	4 [2]	(8)	80/4	>99	98 (1)
13 ^c	1 [2]	(8)	80/4	27	—
14 ^c	2 [2]	(8)	80/4	25	—
15 ^c	3 [2]	(8)	80/4	21	—
16 ^c	5 [2]	(8)	80/4	59	50 (6)
17 ^c	6 [2]	(8)	80/4	60	50 (6)

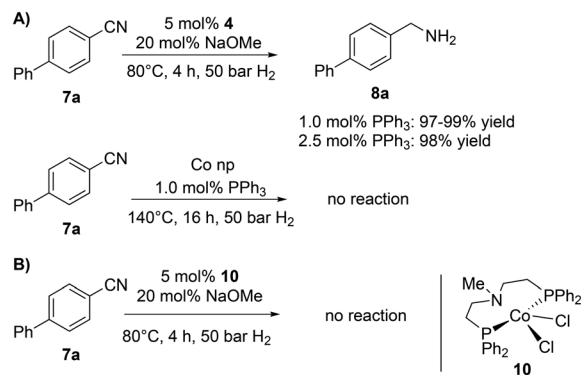
^a 0.5 mmol nitrile, 2–5 mol% 1–6, 8–20 mol% NaOMe, 2 mL dioxane, 50 bar H_2 . ^b Yield determined with an internal standard. Yield of side product **9a** in parentheses. ^c 8 mol% NaBHET_3 .



Before investigating the scope and limitations of the catalytic system, we studied the real nature of the catalytically active species. As demonstrated in the initial experiments, the homogeneous cobalt complex **4** easily forms Co nanoparticles, which are active, similar to their homogeneous counterparts but with lower selectivity (entry 4). These findings are in agreement with the research works of the groups of Jones^{15c} and Guan,^{17e} who also observed the formation of Co nanoparticles at higher temperatures. Therefore, the kinetic profile of the model reaction was recorded, applying Co PNP pincer complex **4** at 80 °C (Fig. 2). In the case of nanoparticle catalysis, a sigmoidal reaction curve is expected with a significant initiation phase caused by the transformation processes of the catalyst.¹⁸ After a heating up period of 10 minutes in the autoclave, the catalytic reaction started forming first the secondary imine **9a** which was immediately transformed into the primary amine **8a**. The monitoring of the concentration/time relationship for the reduction of 4-phenylbenzonitrile (**7a**) showed no significant induction period or break in the reaction curve, which is strong evidence for a homogeneously mediated reaction. Nevertheless, two reaction pathways based on a homogeneous catalyst as well as on nanoparticles could proceed in parallel.

Additionally, poisoning experiments with suitable scavengers such as PPh₃ were performed.¹⁹ In the case of a Co nanoparticle catalyzed reaction, sub-stoichiometric amounts of phosphine are expected to block the active sites of the catalyst and suppress the reaction.¹⁸ However, the hydrogenation of 4-phenylbenzonitrile in the presence of 1 or 2.5 mol% PPh₃ and 5 mol% Co PNP pincer complex **4** at 80 °C formed the primary amine **8a** in 97–99% yield (Scheme 1A). In contrast, the reaction of **7a** with isolated Co nanoparticles formed in our initial experiments was completely stopped in the presence of 1 mol% PPh₃ at 140 °C. These results strongly indicate the homogenous character of the pre-catalyst **4**.

Next, catalytic experiments were realized to learn more about the possible mechanism (Scheme 1B). Here, a charac-



Scheme 1 A) Reduction of 4-phenylbenzonitrile with Co pincer complex **4** or Co nanoparticles in the presence of different amounts of PPh₃. B) Reduction of 4-phenylbenzonitrile with *N*-methylated Co pincer complex **10**.

teristic aspect of pincer complex based catalysis is the ability of the ligand to play an active role in the reaction.²⁰ This metal–ligand cooperation (MLC) was already observed for iron^{11a,b} or manganese¹² catalyzed nitrile reduction including an aliphatic pincer ligand, where the NH moiety was involved in the hydrogen transfer step during the catalysis. When no reaction takes place with the respective pincer catalyst, which is blocked in the NH position, an outer-sphere mechanism is proposed.

Therefore the *N*-methylated Co pincer complex **10** was applied for the catalytic reduction of 4-phenylbenzonitrile, showing no activity at all.²¹ Based on this result, we postulated an outer-sphere mechanism for the catalytic hydrogenation of nitriles catalyzed by Co PNP pincer complex **4** (see the ESI†).

Finally, we investigated the general applicability of Co PNP complex **4** (4 mol% catalyst, 16 mol% NaBHET₃, 80 °C, 50 bar H₂, 6 h). As shown in Scheme 2, various aromatic and heteroaromatic nitriles were smoothly reduced to the corresponding primary amines in good to excellent yields. Compared to the previously reported Co catalyst systems A–C, these are very mild reaction conditions for nitrile reduction. In particular, *para*-substituted substrates (**7c–h**) are reduced in high yields to primary amines; although besides **8d** traces of benzylamine were also detected. Nitriles bearing an *ortho*-substituent on the phenyl ring (**7n**, **7o**, and **7p**) gave lower yields compared to the *para*- or *meta*-substituted substrates. However, with a longer reaction time (16 hours), the product yields increased to 91–93%. The dinitrile **7t** was reduced to the corresponding diamine in 88% yield and 3-cyanopyridine **7l** was converted into 70% of amine **8l**. Carbonyl moieties are not stable under the applied reaction conditions. Here, hydrogenation of the aldehyde (**8i**), ketone (**8j**) and ester groups (**8k**) took place parallel to the reduction of the nitrile group. Exemplarily, two aliphatic nitriles **7u** and **7v** were hydrogenated, too. In these cases, a somewhat longer reaction time (16 h) and higher reaction temperature (100 °C) were required to obtain moderately higher product yields.

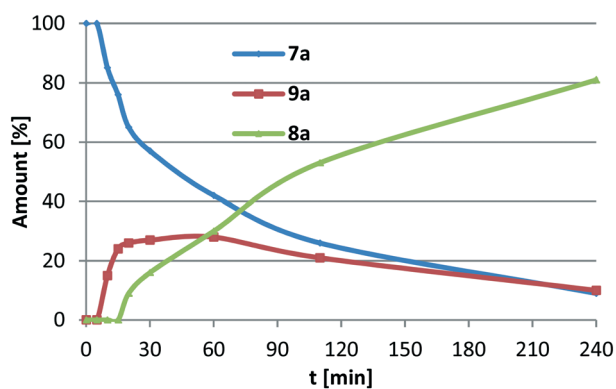
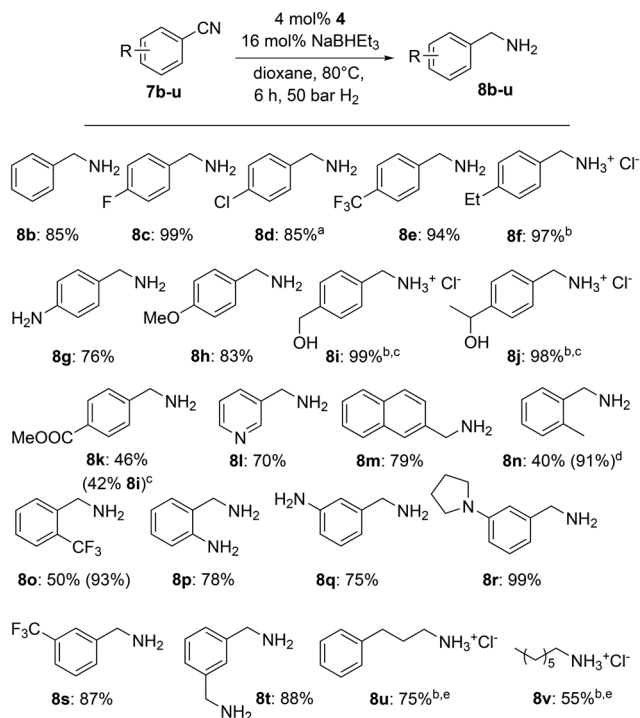


Fig. 2 Concentration/time diagram for the hydrogenation of 4-phenylbenzonitrile (**7a**) catalysed by Co pincer complex **4** at 80 °C.



^a 5% dehalogenation; ^b isolated yield as HCl adduct; ^c both functional groups are reduced; ^d yield after 16 h and 80°C; ^e yield after 16 h and 100°C.

Scheme 2 Substrate scope for nitrile reduction with Co pincer complex **4**.

Conclusions

We have developed a Co catalyst with an aliphatic PNP pincer ligand for the reduction of aromatic and aliphatic nitriles to primary amines. Compared to known cobalt hydrogenation catalysts, complex **4** operates under milder reaction conditions. Mechanistic experiments indicate a homogeneous character of this catalyst system.

Conflicts of interest

There are no conflicts to declare.

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