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Selective hydrogenation of nitriles to primary amines using a new cobalt phosphine catalyst

Rosa Adam,^[a] Charles Beromeo Bheeter,^[a] Jose R. Cabrero-Antonino,^[a] Kathrin Junge,^[a] Ralf Jackstell^[a] and Matthias Beller^{*[a]}

Abstract: A general protocol for the catalytic hydrogenation of nitriles to primary amines using a non-noble metal based system is presented. Co(acac)₃ in combination with tris(2-(dicyclohexylphosphanyl)ethyl) phosphane **L3** catalyses efficiently the selective hydrogenation of a wide range of (hetero)aromatic and aliphatic nitriles to the corresponding amines.

Amines are valuable compounds present in many agrochemicals and drugs. In addition, many other industrially relevant products, such as dyes, detergents, solvents, additives or anti-foam agents contain amines in their structure.^[1] More specifically, primary amines are highly relevant due to their straightforward functionalization.^[2] Among the currently known methodologies for the synthesis of primary amines,^[3] nitriles reduction constitutes a particularly useful and atom-economical approach. Traditionally in organic synthesis, nitriles have been reduced using metal hydrides such as LiAlH₄ or NaBH₄.^[4] Despite being useful on laboratory scale, these methodologies present important drawbacks in terms of selectivity and generation of waste. In contrast, hydrogenation of nitriles is a greener approach as it is more sustainable and atom-efficient.^[5]

On an industrial level, the hydrogenation of nitriles is performed using heterogeneous catalysts, mainly Raney® -Ni and -Co.^[6] However, these catalysts are highly sensitive and sometimes show poor selectivities. To overcome these limitations, in the last years many academic and industrial efforts are focussed to find improved catalytic systems able to mediate this important transformation. Most of the developed homogeneous catalysts are based on precious metals such as Ru,^[7] Rh,^[8] Ir^[9] or Re.^[10] Nevertheless, nowadays one of the major goals in catalysis is the replacement of such precious metals by inexpensive and less toxic non-noble metals.^[11] Due to this interest, intensive work is being devoted to design novel systems based in Fe,^[12] Co,^[12a, 13] Mn,^[14] etc. for the hydrogenation of polar bonds such as carbonyl compounds, imines, esters, carboxylic acids or *N*-heterocycles. However, for the particular case of nitriles hydrogenation, only a few examples of non-noble metal based catalysts are known, all of them being pincer type complexes.^[15] Specifically, three iron based catalysts have been reported by the group of Milstein^[16] and our group.^[17] In addition, two more examples in which cobalt^[18] or manganese^[19] complexes were used have also been described. Recently, the first cobalt

catalysed chemodivergent transfer hydrogenation of nitriles was reported.^[20] Despite all these works, base metal complexes with non-pincer type ligands able to catalyse the hydrogenation of nitriles are basically unknown. In this respect, we report here a new efficient cobalt/tetradentate phosphine catalytic system for the synthesis of primary amines from nitriles.

Previous experience in our group in the field of non-noble metal-catalysed hydrogenation and dehydrogenation involved the key use of tetradentate phosphine-type ligands in the presence of iron or cobalt metal salts.^[21] Based on this works, we explored the cobalt catalysed hydrogenation of benzonitrile **1**. Initially, three tetradentate ligands **L1-L3** and the tridentate Triphos **L4** (Triphos = 1,1,1-tris(diphenylphosphinomethyl) ethane) were screened (Figure 1) in the presence of Co(acac)₃ (5 mol%), KO^tBu (10 mol%) at 100 °C, under 30 bar of H₂ and using *t*BuOH as solvent during 18 h. Using commercially available ligands **L1** and **L4** no desired product was detected (Table S1, entries 1 and 4). To our delight, tris(2-(dicyclohexylphosphanyl)ethyl) phosphane **L3** afforded benzyl amine **2** in quantitative yields under these conditions (Table S1, entry 3), while **L2** showed some activity (Table S1, entry 2).

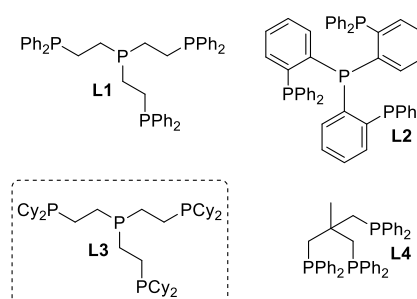


Figure 1. Tri and tetradentate phosphine type ligands used in the screening.

To the best of our knowledge, this is the first example in which tetradentate phosphine **L3** has been used for a catalytic hydrogenation.

Next, the benchmark reaction was performed using different catalyst amounts (Table S1, entries 5 and 6), concluding that a minimum loading of 4 mol% is needed so that the reaction proceeds efficiently. Among the cobalt precursors tested, Co(acac)₃ gave the highest conversion and selectivity to benzyl amine **2** (Table S2). Notably, Co(BF₄)₂·6H₂O and Co(OAc)₂ (Table S2, entries 3 and 6) also afforded high conversions but with low selectivities to benzyl amine **2**. Further investigations on the influence of pressure and temperature parameters (Table S1, entries 7-9) allowed us to mitigate the reaction temperature to 80 °C using 30 bar of H₂.

Several control experiments were performed (Table S1, entries 10-13) demonstrating that the presence of Co(acac)₃, ligand **L3** and KO^tBu were required to obtain good yields of benzyl

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amine **2**. In addition, the influence of base in the reaction was studied (Table S3). A base loading of 10 mol% or higher prevented the formation of N-benzyl-1-phenylmethanimine **S1**, detected at lower base loadings. Formation of secondary imine **S1** is explained by the attack of benzyl amine **2** to the primary imine intermediate. This process occurs with the simultaneous release of ammonia, and hence, is avoided through the base addition. It should be noted that when the reaction was performed with 20 mol% of KOtBu (Table S3, entry 7) or in the absence of Co(acac)₃ (Table S1, entry 12) considerable amounts of benzamide **S2** were detected.^[22]

Then, the influence of different solvents under the optimized reaction conditions was assessed (Table S4). Interestingly, the catalyst only worked in alcohol type solvents and the presence of water completely inhibited its activity. Primary and secondary alcohols afforded lower selectivities to the desired amine **2** in comparison with tBuOH.

At this point we were interested to understand our catalytic system in more detail. Hence, yield/time kinetic profiles for the hydrogenation of **1** in the presence of Co(acac)₃/L3 system at 80 and 100 °C were performed (Figure 2). A comparison of both profiles reveals a clear induction period at 80 °C, which is not detected at 100 °C. This effect is attributed to a slower formation of the catalytic active species at lower temperatures due to the difficulty in removing acac ligands.^[23] In fact, ESI-MS tests performed in aliquots of the 80 °C reaction at 30 and 60 minutes detected the presence of [Co(acac)₃+Na]⁺ (m/z = 379.056), which disappeared at longer reaction times (Figures S1-S3). In addition, at 1 and 2.5 hours [Co(L3)tBuOH]⁺ (m/z = 839.516) was detected (Figures S2 and S3). Furthermore, a ³¹P NMR comparison of the reaction mixtures at 80 and 100 °C at 1 and 2.5 hours revealed at both reaction times the presence of an increased amount of coordinated phosphorous ligands at higher temperature (Figures S4 and S5). To gain further evidences, a pre-heating of the catalyst solution under 30 bar of H₂ at 80 °C was performed during 1.5 hours before adding benzonitrile **1**. Under these conditions, a mitigation of the induction period was observed (Figure S6) indicating a faster formation of the catalyst active species.

Having the optimized conditions in hand, the general applicability of this cobalt catalysed protocol was demonstrated through the hydrogenation of a series of (hetero)aromatic substrates (Table 1). Most of the compounds could be hydrogenated at 80-120 °C in the presence of 4 mol% of cobalt, 10 mol% KOtBu under 30 bar of H₂. Electron-releasing (Table 1, entries 3-10) as well as electron-withdrawing (Table 1, entries 11-14) substituted benzonitriles were successfully converted. A clear correlation between the electronic nature of the substituent and the required reaction temperature was not observed. By contrast, electron-releasing *meta*-substituted benzonitriles could be hydrogenated at milder reaction conditions compared with *ortho*- and *para*- substituted ones (Table 1, entries 4-5 and 8-10). Interestingly, no hydrogenation of amides occurred under these conditions (Table 1, entry 15), while for methyl 4-cyanobenzoate complicated mixtures were obtained.

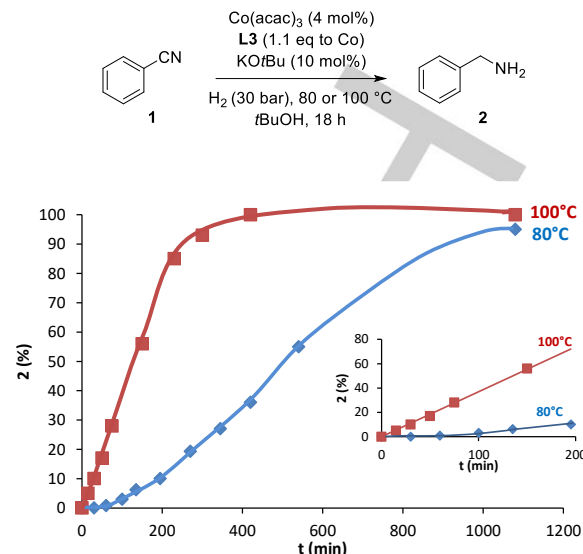


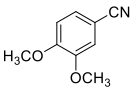
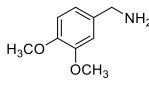
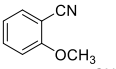
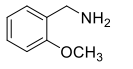
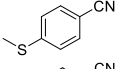
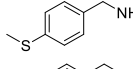
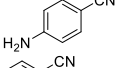
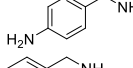
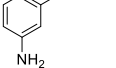
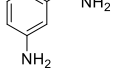
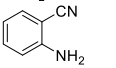
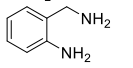
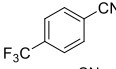
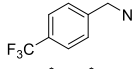
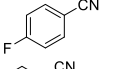
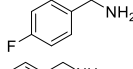
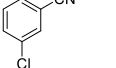
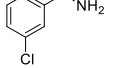
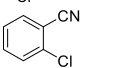
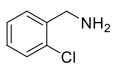
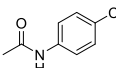
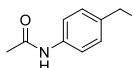
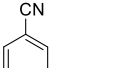
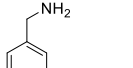
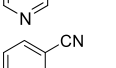
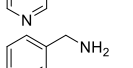
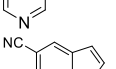
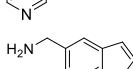
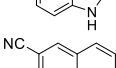
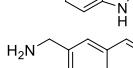
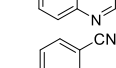
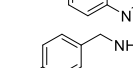
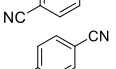
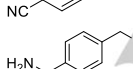
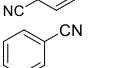
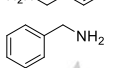
Figure 2. Yield/time kinetic profile for the hydrogenation of benzonitrile **1** to benzyl amine **2** with Co(acac)₃/L3 at 80 °C (blue line) and 100 °C (red line).

In addition, the hydrogenation of selected N-containing heteroaromatic nitriles was achieved (Table 1, entries 16-19). For example, 4-pyridinecarbonitrile was successfully hydrogenated at 80 °C (Table 1, entry 16). In the case of 3-pyridinecarbonitrile and 6-quinolinecarbonitrile 120 °C were required for obtaining good yields (Table 1, entries 17 and 19), while 140 °C and a higher catalyst loading were needed for 1H-indole-5-carbonitrile (Table 1, entry 18). Moreover, the Co(acac)₃/L3 system catalysed the hydrogenation of terephthalodinitrile and isophthalodinitrile at 120 °C, affording the corresponding diamines in good isolated yields (Table 1, entries 21 and 22). Notably, the selective monohydrogenation of terephthalodinitrile could also be achieved by performing the reaction under milder conditions (80 °C; Table 1, entry 20).

Table 1. Hydrogenation of various aromatic nitriles.^[a]

$\text{Ar-CN} \xrightarrow[\text{tBuOH, 18 h}]{\text{Co(acac)}_3 \text{ (4 mol\%)}, \text{L3 (1.1 eq to Co)}, \text{KOtBu (10 mol\%)}, \text{H}_2 \text{ (30 bar), T (}^\circ\text{C)}} \text{Ar-CH}_2\text{NH}_2$					
Entry	Nitrile	Amine	T (°C)	Conv. (%) ^[b]	Yield (%) ^[c]
1			80	100	99 ^[e]
2 ^[c]			120	100	98
3			80	100	98
4			100	100	97

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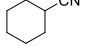
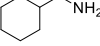

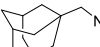


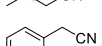
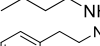
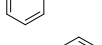
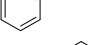
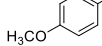
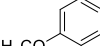
5			80	100	96
6			100	100	76
7 ^[d]			120	100	77 ^[e]
8			120	100	97
9			100	100	83
10 ^[c]			120	100	86
11			100	100	99
12			100	100	96
13			120	100	86
14			120	100	87
15			80	100	96 ^[e]
16			80	100	99
17			120	100	98
18 ^[c]			140	100	79
19			120	100	86 ^[e]
20			80	100	61 ^[e]
21			120	100	80 ^[e]
22 ^[d]			120	100	79 ^[e]

[a] Standard reaction conditions: nitrile (0.25 mmol), Co(acac)₃ (4 mol%), **L3** (4.4 mol%), KO^tBu (10 mol%), dry *t*BuOH (2 ml) under 30 bar of H₂ during 18 h. [b] Conversion and yield were calculated by GC using hexadecane as external standard. [c] Co(acac)₃ (8 mol%). [d] Run at 48 h. [e] Yield of product isolated as the ammonium salt.

With the aim of extending the cobalt catalysed protocol for the hydrogenation of aliphatic nitriles, a further optimization of the reaction conditions was performed using octanenitrile as model substrate (Table S5). A variety of aliphatic nitriles could be hydrogenated at 140°C, 30 bar of H₂, 5 mol% of cobalt and 10 mol% of KO^tBu during 24 hours (Table 2). Under these conditions aliphatic nitriles bearing a short alkyl chain, cyclic nitriles, and 3-phenylpropanenitrile were successfully hydrogenated (Table 2,

entries 1-3, 7-8 and 12). In the case of nitriles bearing longer alkyl chains, branched or benzylic, either higher catalyst loadings or longer reaction times were required (Table 2, entries 4-6 and 9-11).

Table 2. Hydrogenation of various aliphatic nitriles.^[a]

$\text{R}-\text{C}\equiv\text{N} \xrightarrow[\text{H}_2 \text{ (30 bar), 140 }^\circ\text{C, } t\text{BuOH, 24 h}]{\text{Co(acac)}_3 \text{ (5 mol\%)} \\ \text{L3 (1.1 eq to Co)} \\ \text{KO}^t\text{Bu (10 mol\%)}} \text{R}-\text{CH}_2\text{NH}_2$				
Entry	Nitrile	Amine	Conv. (%) ^[b]	Yield (%) ^[b]
1	C ₄ H ₉ CH ₂ CN	C ₄ H ₉ CH ₂ CH ₂ NH ₂	100	83
2	C ₅ H ₁₁ CH ₂ CN	C ₅ H ₁₁ CH ₂ CH ₂ NH ₂	100	99
3	C ₆ H ₁₃ CH ₂ CN	C ₆ H ₁₃ CH ₂ CH ₂ NH ₂	100	91
4 ^[c]	C ₈ H ₁₇ CH ₂ CN	C ₈ H ₁₇ CH ₂ CH ₂ NH ₂	100	99
5 ^[c]	C ₁₀ H ₂₁ CH ₂ CN	C ₁₀ H ₂₁ CH ₂ CH ₂ NH ₂	100	98
6 ^[c]	C ₁₅ H ₃₁ CH ₂ CN	C ₁₅ H ₃₁ CH ₂ CH ₂ NH ₂	100	70 ^[e]
7			100	99
8			100	90
9 ^[c]			100	92
10 ^[d]			100	71
11 ^[d]			100	87
12			100	89

[a] Standard reaction conditions: nitrile (0.25 mmol), Co(acac)₃ (5 mol%), **L3** (5.5 mol%), KO^tBu (10 mol%), dry *t*BuOH (2 ml) under 30 bar of H₂ during 24 h. [b] Conversion and yield were calculated by GC using hexadecane as external standard. [c] Run at 48 h. [d] Co(acac)₃ (8 mol%). [e] Yield of product isolated as the ammonium salt.

In conclusion, we describe the first molecularly-defined non-pincer base metal catalyst, which is able to selectively hydrogenate nitriles to primary amines. A variety of (hetero)aromatic and aliphatic nitriles are hydrogenated with good to excellent yields using this convenient in situ generated non-noble metal system. Mechanistic investigations indicate a strong dependence on temperature for the formation of the active catalytic Co/**L3** species.

Experimental Section

General procedure for benzonitrile hydrogenation with [Co]/L3**:** A 4 mL glass vial containing a stirring bar was charged with Co(acac)₃ (3.6 mg, 0.01 mmol, 4 mol%) and **L3** (7.3 mg, 0.011 mmol, 4.4 mol%). The vial, sealed with a septum equipped with a syringe needle, was evacuated and subsequently flushed with argon three times. Dry *tert*-butanol (2 mL)

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and benzonitrile **1** (0.25 mmol) were added under argon. The mixture was stirred until the compounds were completely dissolved forming a green solution. Then, KO^tBu (2.8 mg, 0.025 mmol, 10 mol%) was added observing a colour change to brown. The vial was set in an alloy plate and introduced into a 300 mL autoclave filled with argon. The autoclave was sealed, purged (20 bar of H₂, three times) and pressurized with H₂ (30 bar). Then the autoclave was seated in an aluminum block on a stirring machine and heated to 80 °C for 18 hours. After that the reaction mixture was cooled in cold water and the gas carefully released. The reaction mixture was analyzed by GC-MS and GC with n-hexadecane as an internal standard.

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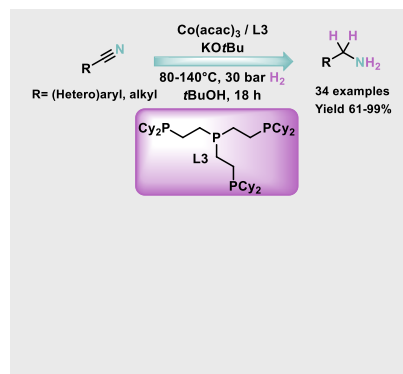
Keywords: Cobalt • homogeneous catalysis • hydrogenation • nitrile • phosphines

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Cobalt catalyzes it: A general protocol for the hydrogenation of nitriles using a cobalt based system is described. The use of the tetradentate ligand **L3** is the key for the activity of the system.



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Selective hydrogenation of nitriles to
primary amines using a new cobalt
phosphine catalyst