

Homogeneous Catalysis

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A General and Highly Selective Cobalt-Catalyzed Hydrogenation of N-Heteroarenes under Mild Reaction Conditions

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Dedicated to Professor Belén Abarca on the occasion of her 70th birthday

Abstract: Herein, a general and efficient method for the homogeneous cobalt-catalyzed hydrogenation of N-heterocycles, under mild reaction conditions, is reported. Key to success is the use of the tetradentate ligand tris(2-(diphenylphosphino)phenyl)phosphine). This non-noble metal catalyst system allows the selective hydrogenation of heteroarenes in the presence of a broad range of other sensitive reducible groups.

Homogeneous hydrogenation of arenes is a challenging transformation because of the stability derived from the aromaticity. In the particular case of N-heteroarenes, this process not only has to overcome the resonance stability, but also the possible poisoning of the catalyst by either the starting material or the product.^[1] Nevertheless, significant developments took place in the past decades and many applications are known for the hydrogenation of model N-heterocycles. Among the various N-heterocycles, compounds containing a 1,2,3,4-tetrahydroquinoline structure and related ones are ubiquitous in natural products. Hence, many bioactive compounds based on this scaffold are used as drugs and agrochemicals.^[2] In fact, oxamniquine^[3] and flumequine^[4] are currently in use as antihelmintic and antibacterial agents, respectively. Moreover, the (de)hydrogenation of N-heterocycles is of interest for hydrogen storage.^[5]

In general, heterogeneous catalysts have been developed for this transformation and most of them are based on precious metals, which sometimes have selectivity issues (Figure 1 a).^[6] More recently, non-noble metal catalysts have been applied: For example, supported cobalt nanoparticles have been shown to efficiently hydrogenate N-heteroarenes at >100 °C, but the chemoselectivity in the presence of additional reducible groups is still a limitation (Figure 1 a).^[7] In contrast, homogeneous catalysts allow hydrogenation at milder reaction conditions. Most of these systems are based

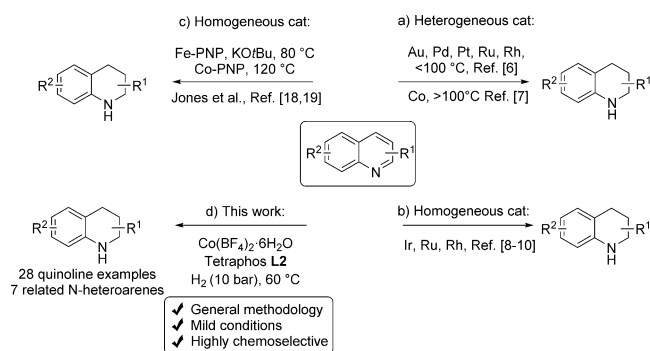


Figure 1. Reported examples of quinoline hydrogenation using: a) heterogeneous catalysts; b) homogeneous catalysts of Ir, Ru, or Rh; c) homogeneous catalysts of either Fe- or Co-PNP complexes; d) [Co]/L2 homogeneous catalyst reported in this work.

on either Ir,^[8] Rh,^[9] or Ru,^[9a,10] and some of them require the use of additives, such as I₂ (Figure 1 b).^[8a,11]

The replacement of precious metals by earth-abundant, first-row metals, is contemporary and highly desirable in terms of sustainability.^[12] In the last decade important advances in the scientific community have been reported.^[13] Major works are concerned with the use of iron-based catalysts for the hydrogenation of alkenes, aldehydes, ketones, imines, nitriles, and carboxylic acid derivatives.^[14] In addition, important work for the development of new cobalt^[15] and manganese^[16] hydrogenation catalysts has been done. In the particular case of N-heteroarenes, elegant work by Jones and co-workers showed that iron^[17] and cobalt^[18] catalysts are able to perform acceptorless catalytic dehydrogenation and hydrogenation of N-heterocycles (Figure 1 c).

Herein, we report the first general protocol for the chemoselective hydrogenation of quinolines and related heterocycles, based on a nonprecious metal, under mild reaction conditions and with a high tolerance for other reducible groups (Figure 1 d).

Encouraged by the previous experiences within our group regarding cobalt- and iron-catalyzed hydrogenation and dehydrogenation reactions using tetradentate phosphine-type ligands,^[19] we became interested in the cobalt-catalyzed hydrogenation of quinoline (**1a**). In a first approach, several phosphines were tested in the presence of Co(BF₄)₂·6H₂O (5 mol %), under 50 bar of H₂, at 100 °C in THF (tetrahydrofuran) during 15 hours (Figure 2). Commercially available tridentate (**L4** and **L5**), as well as bidentate (**L6** and **L7**)

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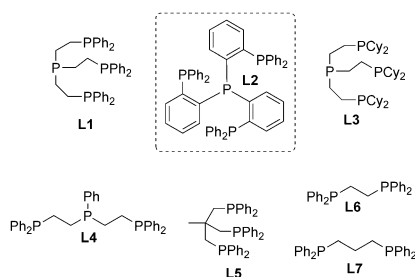


Figure 2. Bi-, tri-, and tetradentate phosphines screened in this work.

ligands did not show any activity under the studied reaction conditions (see Table S1, entries 4–7 in the Supporting Information). Unfortunately, **L1**, which is also useful for Ru-, Fe-, and Co-catalyzed hydrogenation of polar bonds, showed very little activity (Table S1, entry 1). However in contrast, the modified tetradentate ligand tris(2-(diphenylphosphino)phenyl)phosphine (**L2**) afforded the desired 1,2,3,4-tetrahydroquinoline (**2a**) in high yield (98%; Table S1, entry 2). Interestingly, the related tetraphos-type ligand **L3** gave no desired product (Table S1, entry 3). Remarkably, the [Co]/**L2** system works in the absence of any acid additive, which was needed in previously described [Fe]/**L2** hydrogenation systems.^[19c,f]

A systematic investigation of the pressure and temperature parameters using the [Co]/**L2** system revealed the efficient hydrogenation of quinoline at 60 °C under only 10 bar of H₂ (Table S1, entries 8–12). To the best of our knowledge this class of hydrogenations have not been achieved under such mild reaction conditions using base metal catalysts. Next, several metal precursors were tested for the benchmark reaction (Table S2). Among the cobalt precursors studied, Co(BF₄)₂·6H₂O resulted the most active one, although Co(ClO₄)₂·6H₂O also presented a remarkable activity (> 99 and 79% conv., Table S2, entries 1 and 2). In addition, tetrafluoroborate salts of other nonprecious metals were explored, but only little activity (12% conv.) was observed in the case of the iron salt (Table S2, entries 11–13).

At this point, the influence of several solvents on the reaction was assessed (Table S3). In general, good yields were obtained with polar solvents (Table S3, entries 1–6), with the best results in the case of THF (> 99% conv., Table S3, entry 1). Notably, the catalyst system is tolerant to water. Hence, its addition resulted only in a slight drop of the activity (86% conv., Table S3, entry 2), while in toluene, the system was inactive (entry 7). Finally, the reaction was tested using different catalyst loadings (Table S1, entries 16 and 17), and it was discovered that 3 mol % of the cobalt catalyst is sufficient for full conversion.

Once we had the optimal reaction conditions in hand, we tried our method with the isolated complex. Following the previously described protocol for a related iron complex^[19d] (see the Supporting Information), we obtained the [CoF(**L2**)](BF₄) complex **3**, having one fluorine ligand derived from the original BF₄[−] anion. X-ray analysis revealed that the cobalt center presents a distorted trigonal bipyramidal coordination sphere (Figure 3). Although different cobalt

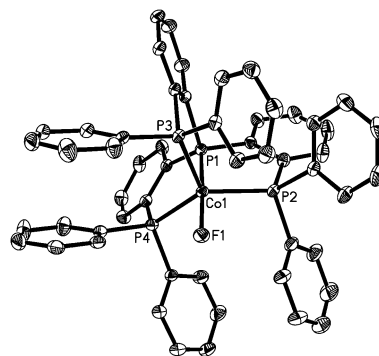


Figure 3. Molecular structure of the cation of [CoF(**L2**)](BF₄) (**3**) in the crystal.^[23] Hydrogen atoms have been omitted for clarity. Displacement ellipsoids correspond to 30% probability.

complexes of **L2** have been analytically characterized,^[20] to the best of our knowledge, no catalytic experiments have been reported. The new complex **3** afforded excellent results for the hydrogenation of **1a** comparable to the in situ system (Table S1, entry 18).

With the aim of studying the generality of the protocol, several substituted quinolines were reacted using the [Co]/**L2** system (Table 1). Both, electron-releasing and electron-withdrawing groups were well tolerated. In the case of 6-substituted and 8-substituted quinolines, hydrogenation proceeded smoothly under mild reaction conditions (entries 2–9 and 11), and the corresponding 1,2,3,4-tetrahydroquinolines

Table 1: Cobalt-catalyzed hydrogenation of substituted quinolines.^[a]

$\text{R} \begin{array}{c} \text{---} \text{Quinoline} \text{---} \text{R}' \end{array} \xrightarrow[\text{THF, 15 h}]{\text{Co(BF}_4)_2 \cdot 6\text{H}_2\text{O (3 mol\%)} \\ \text{L2 (3 mol\%)} \\ \text{H}_2 \text{ (10 bar), } T} \text{R} \begin{array}{c} \text{---} \text{1,2,3,4-tetrahydroquinoline} \text{---} \text{R}' \end{array}$				
Entry	Quinoline 1	<i>T</i> [°C]	Conv. [%] ^[b]	2 Yield [%] ^[b]
1		60	> 99	2a , 89
2		60	> 99	2b , 85
3		60	> 99	2c , 91
4		60	> 99	2d , 95
5		80	> 99	2e , 82
6		80	95	2f , 90
7		60	> 99	2g , 95
8		80	95	2h , 84
9		80	> 99	2i , 91

Table 1: (Continued)

Entry	Quinoline 1	T [°C]	Conv. [%] ^[b]	2 Yield [%] ^[b]
10		120	> 99	2j , 98
11		60	> 99	2k , 95
12 ^[c]		60	98	2l , 79
13 ^[c]		60	> 99	2m , 91
14 ^[c]		60	> 99	2n , 85
15		80	92	2o , 88
16		100	90	2p , 82
17 ^[c]		100	97	2q , 94
18 ^[c,d]		100	> 99	2r , 96
19 ^[c]		100	84	2s , 78
20 ^[e]		130	98	2t , 85

[a] Standard reaction conditions: Substrate (0.25 mmol), Co(BF₄)₂·6H₂O (3 mol %), **L2** (M/L, 1:1), THF (2 mL), H₂ (10 bar), 60–130 °C, 15 h.

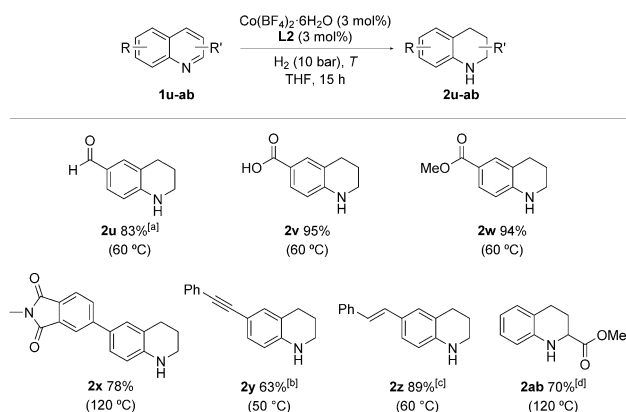
[b] Conversion of the starting material was calculated by GC using hexadecane as internal standard. Yield of isolated product given.

[c] Co(BF₄)₂·6H₂O (5 mol %). [d] Run at 40 h. Total hydrogenation of both rings was detected obtaining a d.r. (racemic/meso) = (69:31).

[e] Co(BF₄)₂·6H₂O (8 mol %).

were isolated in good to excellent yields. The only exception was 8-aminoquinoline (**1j**), which required 120 °C, probably because of its more favorable coordination to the metal center. Remarkably, the quinaldines **1l–o** were also successfully hydrogenated (entries 12–15). Furthermore, the 2-substituted more sterically hindered quinolines **1p** and **1q** were hydrogenated at 100 °C (entries 16 and 17). 2,2-Biquinoline (**1r**) reacted simultaneously at both pyridine rings at 100 °C (entry 18) using 5 mol % of cobalt and a longer reaction time. 3- and 4-methyl quinolines (**1s** and **1t**), wherein the latter example is commonly known as a challenging substrate,^[7a,21] were successfully hydrogenated in good to excellent yield, albeit with higher catalyst loadings and temperatures.

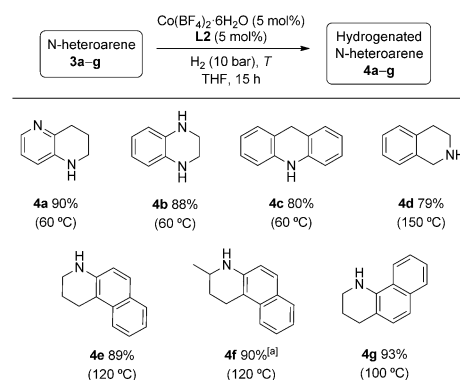
Then, we explored the selectivity of this cobalt system in the hydrogenation of several quinolines bearing other reducible groups (Scheme 1). Gratifyingly, the [Co]/**L2** system hydrogenated the heteroarene selectively in the presence of not only esters, a carboxylic acid, or a cyclic imide, but also



Scheme 1. [Co/**L2**]-catalyzed selective hydrogenation of different quinolines containing reducible groups. Standard reaction conditions: substrate (0.25 mmol), Co(BF₄)₂·6H₂O (3 mol %), **L2** (M/L, 1:1), THF (2 mL), and H₂ (10 bar) at the noted temperature, 15 h. Yield of product given. [a] Co(BF₄)₂·6H₂O (4 mol %). [b] Traces of 6-styryl-1,2,3,4-tetrahydroquinoline were detected. The moderate yield of isolated **2y** is due to degradation problems. [c] Traces of 6-phenethyl-1,2,3,4-tetrahydroquinoline were detected. [d] Co(BF₄)₂·6H₂O (5 mol %).

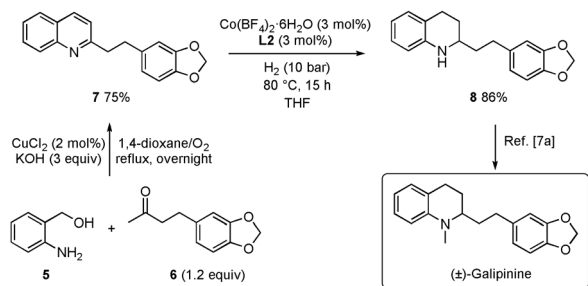
highly sensitive groups such as alkene, alkyne, and aldehyde. To the best of our knowledge such latter heteroarene hydrogenations have not been described. Apparently, this method constitutes a powerful tool for the further functionalization of the corresponding substituted 1,2,3,4-tetrahydroquinolines.

From the viewpoint of organic synthesis, it is interesting that the protocol could also be extended to the hydrogenation of other important N-heteroarenes (Scheme 2). Thus, several heterocycles such as naphthyridine (**4a**), quinoxaline (**4b**), or acridine (**4c**), were hydrogenated at 60 °C, while higher temperatures were required for isoquinoline (**4d**) and the benzoquinolines **4e–g**. In contrast, only moderate or low yields were obtained for various indole and pyridine derivatives (Scheme S5).



Scheme 2. [Co/**L2**]-catalyzed selective hydrogenation of N-heteroarenes. Standard reaction conditions: substrate (0.25 mmol), Co(BF₄)₂·6H₂O (5 mol %), **L2** (M/L, 1:1), THF (2 mL), and H₂ (10 bar) at the noted temperature, 15 h. Yield of isolated product given. [a] Co(BF₄)₂·6H₂O (8 mol %).

As a specific synthetic application, we developed a formal synthesis of (±)-galipinine, a natural product with multiple biological activities.^[22] Preparation of 2-(2-(benzo[d][1,3]-dioxol-5-yl)ethyl)-quinoline (**7**) in a straightforward manner, followed by hydrogenation with [Co]/**L2** under mild reaction conditions gave **8**, which is a direct precursor of this relevant compound (Scheme 3).



Scheme 3. Synthesis of the (±)-Galipinine precursor **8** using the [Co]/**L2**-catalyzed hydrogenation as a key step. Yield of isolated product given.

In conclusion, the first general and highly selective cobalt-catalyzed protocol for the hydrogenation of quinolines and other related N-heterocycles has been developed. The active $\text{Co}(\text{BF}_4)_2/\mathbf{L2}$ system can hydrogenate a variety of N-heteroarenes with good yields under mild reaction conditions. This compound is the first nonpincer base metal complex to catalyze such reactions. Interestingly, the catalyst shows excellent chemoselectivity and hydrogenation of the heteroarene is possible in the presence of other easily reducible groups. This aspect is a substantial advantage in comparison with other methodologies and the demonstrated chemoselectivity opens the door to the alternative synthesis of valuable heterocyclic products.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cobalt · homogeneous catalysis · hydrogenation · nitrogen heterocycles · phosphines

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- [23] CCDC 1523076 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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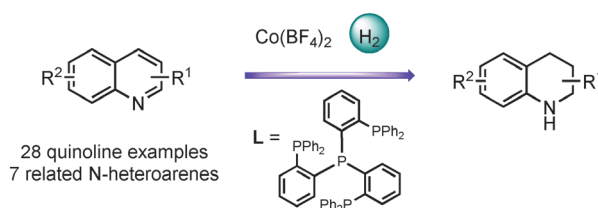
Communications



Homogeneous Catalysis

R. Adam, J. R. Cabrero-Antonino,
A. Spannenberg, K. Junge, R. Jackstell,
M. Beller* ————— ■■■■-■■■■

A General and Highly Selective Cobalt-Catalyzed Hydrogenation of N-Heteroarenes under Mild Reaction Conditions



Reduction! Quinolines and related N-heteroarenes are hydrogenated using [Co]/L. The reactions proceed under mild conditions in a highly selective manner.

