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Nitrile Hydrogenation

Ruthenium/Imidazolylphosphine Catalysis: Hydrogenation of Aliphatic and Aromatic Nitriles to Form Amines

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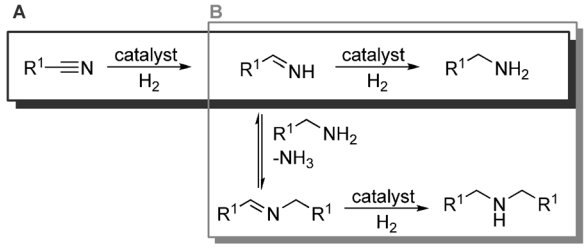
Abstract: A convenient and efficient catalyst system for the hydrogenation of aliphatic nitriles towards the corresponding primary amines in high to excellent yields is presented. In addition, aromatic nitriles are reduced smoothly, too. The use of low catalyst loadings and molecular hydrogen make this protocol an attractive methodology.

Aliphatic amines are of importance as natural and synthetic chemicals in industry and everyday life, especially as pharmaceuticals, agrochemicals, and polymers.[1] On a small scale, the synthesis of amines is often still realized using stoichiometric amounts of metal hydrides such as $LiAlH_4$ or $NaBH_4$. From economic and ecologic points of view, catalytic methods offer more effective and versatile approaches to amines. Here, C–N bond-forming reactions, such as hydroaminations of olefins and alkynes,[1c,2] hydroaminomethylations of olefins,[3] or reductive aminations of carbonyl compounds have been developed. In addition, catalytic reductions of nitriles with molecular hydrogen allow for a clean and atom economic access to amines. As shown in Scheme 1, initially the nitrile forms the corresponding primary imine, which is subsequently hydrogenated to the desired primary amine (path **A**). However, the product can react further on with the imine to give the secondary imine by releasing ammonia (path **B**). Final hydrogenation leads to the secondary amine as a side-product.



Scheme 1. Catalytic hydrogenation of nitriles and possible side reaction.

The selection of the catalyst and reaction conditions is crucial for obtaining high selectivity to the desired primary amines. Basically, all known homogeneous catalyst systems for the hydrogenation of nitriles were developed for the reduction of aromatic nitriles.[4] After the original work by Pez and Grey[4a,b] in the 1980s, further progress applying ruthenium hydride complexes was achieved by Beatty and Paciello,[4i] Frediani et al.,[4j] Morris et al.,[4k] Sabo-Etienne et al.[4l] and Leitner et al.[4m] in the last decades. Moreover, various systems that make use of non-hydride complexes were developed by Dewhirst,[4c] Bianchini et al.,[4d] Hidai et al.[4e] and by our group.[4f–h,n,o]

Here, we present the first general protocol for the catalytic hydrogenation of various aliphatic nitriles by applying a defined ruthenium/imidazolylphosphine-based catalyst system (ligands **1**–**7** are depicted in Figure1).

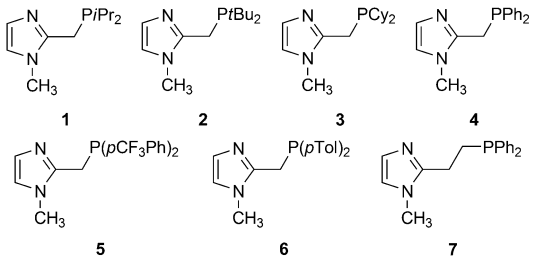


Figure 1. Structure of different imidazolylphosphine ligands tested for the hydrogenation of hexanenitrile.

Recently, we reported the synthesis and successful application of imidazolylphosphine ligands for the Ru-catalyzed hydrogenation of carboxylic esters.[5] The combination of $[\{Ru(benzene)Cl_2\}_2]$ with ligands **3** or **6** gave good to excellent results for the hydrogenation of aromatic, aliphatic and cyclic lactones and carboxylic esters. Although esters were selectively reduced to alcohols in the presence of many functional groups, in case of a nitrile moiety the formation of the corresponding amine was observed. Based on our interest in nitrile reduction[4f–h,n,o] and to the importance of the resulting amines, we started to investigate the potential of the imidazolylphosphine ligands in the Ru-catalyzed hydrogenation of aliphatic nitriles, which represent more challenging substrates.[4m]

At first, different *P,N*-ligands **1**–**7** (Figure 1) were tested in the Ru-catalyzed reduction of hexanenitrile **8b**. Preliminary experiments showed that $[Ru(cod)(methylallyl)_2]$ is a suitable

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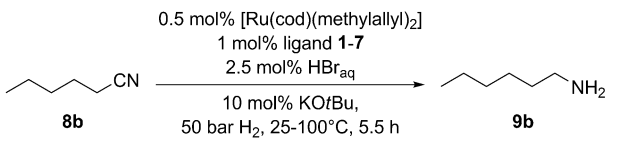
catalyst precursor in this reaction. For convenience, the active catalyst is generated in situ from 0.025 mmol [Ru(cod)(methylallyl)$_2$] and 0.05 mmol ligand **1**–**7**.[6] At 80 °C most of these imidazolylphosphine ligands are able to transform the model nitrile to the desired amine with yields up to 79% (Table 1). In addition to the different substituents on the phosphorus atom in ligands **1**–**6**, a different chain length between the imidazolyl and the phosphorus moiety was investigated. Comparing the results for the Ru-catalyzed hydrogenation of hexanenitrile **8b** with **4** (17%) and **7** (12%), no clear trend is observed. On the other hand, the substituent on the phosphorus has a strong influence on the reaction outcome. In particular, ligands **2** and **3**, bearing alkyl groups on the phosphorus part, gave hexylamine **9b** in high yields (Table 1, entries 2 and 3). Owing to the fact that ligands **2** and **3** led to similar yields, we decided to use **3** for further studies due to the easier preparation.

Table 1. Ru-catalyzed hydrogenation of hexanenitrile in the presence of different phosphine/amine-imidazolyl ligands.[a]



8b **9b**

	Ligand	Ratio	*T* [°C]	Yield [%][b]
1	**1**	1:2	80	35
2	**2**	1:2	80	79
3	**3**	1:2	80	77
4	**4**	1:2	80	17
5	**5**	1:2	80	–
6	**6**	1:2	80	27
7	**7**	1:2	80	12
8	**3**	1:1	80	21
9	**3**	1:4	80	88
10	**3**	1:2	100	93
11	**3**	1:2	40	–
12	**3**	1:2	25	–

[a] Reaction conditions: 5 mmol **8b**, 0.05 mmol **1**-**7**, 0.025 mmol [Ru(cod)(methylallyl)$_2$], HBr$_{aq}$ (48% wt, 0.125 mmol), 0.5 mmol KO*t*Bu, 8 mL toluene, 50 bar H$_2$, *T*, 5.5 h. [b] Yield determined by GC methods using hexadecane as an internal standard.

As shown in Table 1 (entries 3 and 8), by changing the catalyst/ligand ratio from 1:2 to 1:1 the yield dropped down to 21%, whilst a high yield of 88% was observed with a ratio of 1:4 (Table 1, entry 9). Lowering the temperature to 40 and 25 °C (Table 1, entries 11 and 12, respectively) did not lead to any conversion. Best results (93% yield) were obtained when the hydrogenation reaction was performed at 100 °C (Table 1, entry 10). Notably, under our conditions we did not observe the formation of the common side-products (secondary imines and amines). To prove that our reaction proceeds by means of pathway **A**, we hydrogenated benzophenone imine successfully under optimized conditions to get selectively the primary amine.[7]

As described earlier for the hydrogenation of aromatic nitriles,[4f,g] using other bases or even in the absence of base the selectivity to the corresponding primary amine decreases.

To get more insight towards the mechanism we tried to crystallize Ru/imidazolylphosphine complexes. To our delight, for Ru/**4** (compound **10**) and Ru/**3** (compound **11**), crystals suitable for X-ray crystal structure analysis were obtained by overlaying a solution of the complex in dichloromethane with *n*-heptane for several weeks (see the Supporting Information).[8]

As presented in Figure 2, the structures of these two complexes show very different coordination spheres. Complex **10** has one Ru atom in the octahedral coordination sphere with two bidentate imidazolylphosphine ligands **4** and two bromine atoms (Figure 2; top). Considering one bromine atom in the axial position and another one in the equatorial position, the

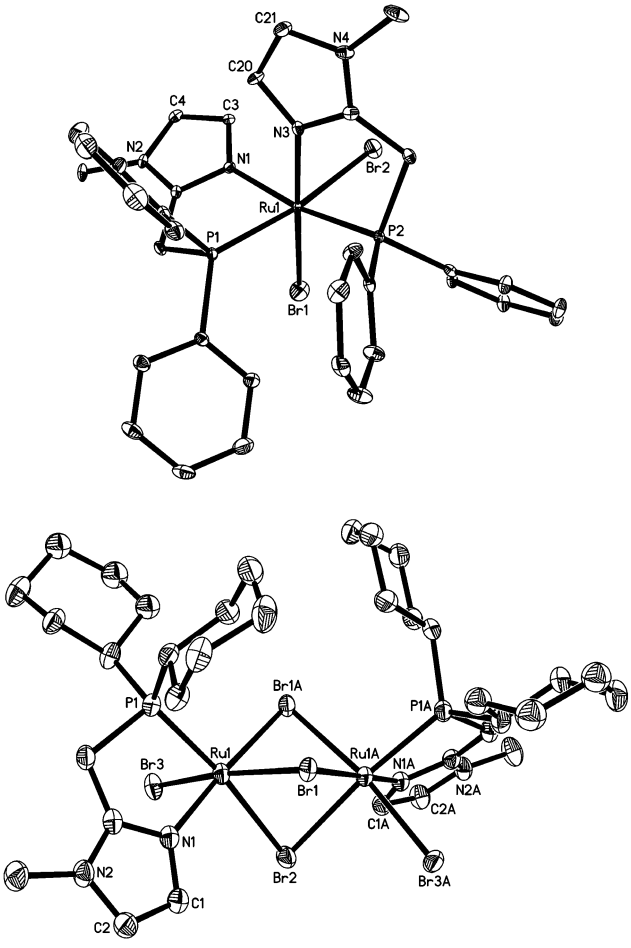


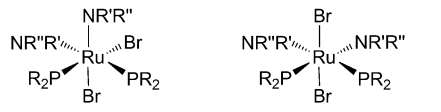
Figure 2. ORTEP representation of **10** (top) and **11** (bottom). Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **10**: N1–Ru1 2.132(5), N3–Ru1 2.080(5), P1–Ru1 2.2500(15), P2–Ru1 2.2731(15), Br1–Ru1 2.5395(9), Br2–Ru1 2.5852(9), N3-Ru1-Br1 175.92(14), P1-Ru1-Br2 167.77(5), N1-Ru1-Br1 87.99(13), P2-Ru1-Br2 88.20(4), Br1-Ru1-Br2 90.96(3); selected bond lengths [Å] and angles [°] for **11**: Br1–Ru1 2.5322(4), Br2–Ru1 A 2.6141(4), Br2–Ru1 2.6141(4), Br3–Ru1 2.4954(4), Br1A–Ru1 2.5090(4), N1–Ru1 2.056(2), P1–Ru1 2.2840(7), Ru1-Br1-Ru1 A 79.176(12), Ru1-Br2-Ru1 A 75.818(15), N1-Ru1-P1 82.44(7), N1-Ru1-Br1 A 175.77(7), P1-Ru1-Br1A 100.68(2), P1-Ru1-Br1 99.99(2), Br3-Ru1-Br1 171.779(13).

two phosphorus atoms are in the equatorial positions, and one nitrogen atom is in the axial position, while another nitrogen atom is in the equatorial position. Counting the number of the valence electrons of complex **10** reveals a Ru^{II} center with 18-electrons in a closed-shell electronic configuration.

In contrast, complex **11** has two Ru centers, which are bridged by three bromine atoms. Each Ru atom bears one additional terminal bromine atom and one bidentate imidazolylphosphine ligand **3** (Figure 2, bottom). Both Ru centers have an octahedral coordination sphere and the two octahedrons are joined on faces of the bridging bromine atoms. Counting the number of the valence electrons of compound **11** reveals one Ru center with 18-electrons and one Ru center with 17-electrons. Therefore, a mixed valence complex of Ru^{II}/Ru^{III+} is assumed. Indeed, Cotton et al.[9] reported very similar structures that bear three bridging chlorine atoms instead of bromine atoms. In addition, the computed energy minimum structure of complex **11** has a C_2 symmetry, indicating that the two Ru centers are equivalent. Thus, complex **11** mimics the Creutz–Taube complex ion,[10] $[C_4H_4N_2]^{5+}[\{Ru(NH_3)_5\}_2]$, which also has two equivalent Ru centers.

As we applied a metal/ligand ratio of 1:2 in the catalytic reaction, complex **10** has two coordinated imidazolylphosphine ligands, while only one imidazolylphosphine ligand is found in complex **11** at each Ru center. This shows that complex **10** is formed as expected, while the formation of complex **11** is rather surprising. One Ru atom in complex **11** is oxidized from Ru^{II} to Ru^{III}, but we started with $[Ru(cod)(methylallyl)_2]$ as an Ru^{II} precursor without the addition of oxidation reagents in our reactions. Therefore, one might consider that such oxidation took place accidentally during the very long crystallization process by air oxygen.

In our NMR measurements with the in situ formed complexes we found two main ^{31}P signals ($\delta = 45.5$, 64.6 ppm) for the complexes with imidazolylphosphine ligand **4** (R = phenyl) and one main signal ($\delta = 37.6$ ppm) for those with imidazolylphosphine ligand **3** (R = cyclohexyl). To understand these results, we carried out BP86 density functional theory computations for the energetics of both types of complexes. Apart from complex **10** with two bromine atoms in *cis*-position (*cis*-**10/4**), we also found one *trans*-isomer (*trans*-**10/4**) (Scheme 2).



cis-**10/4** (R = phenyl) *trans*-**10/4** (R = phenyl)
cis-**10/3** (R = cyclohexyl) *trans*-**10/3** (R = cyclohexyl)

Scheme 2. The *cis*- and *trans*-isomers of **10/4** and **10/3**.

The energy minimum structure of *cis*-**10/4** has C_1 symmetry, while that of *trans*-**10/4** is C_2 symmetrical. The computed Gibbs free energy (ΔG) shows that the *cis*-**10/4** is more stable than *trans*-**10/4** by 0.53 kcal mol^{-1}, which reveals an equilibrium ratio of 70:30. This ratio agrees roughly with the estimated ^{31}P NMR intensities.

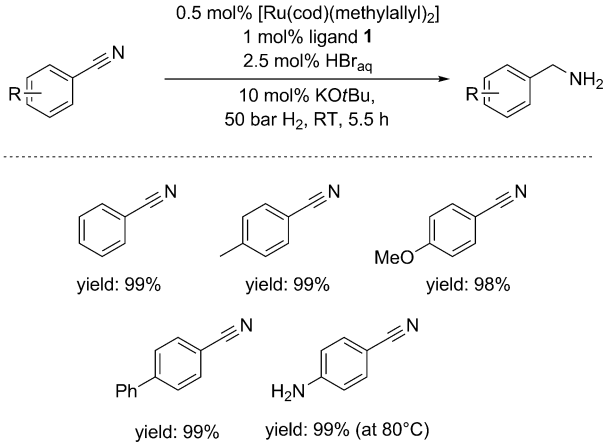
For the expected monoruthenium complex with two bidentate imidazolylphosphine ligands **3** (R = cyclohexyl) and two bromine atoms which mimics complex **10/4**, we also calculated the *cis*-**10/3** and *trans*-**10/3** isomers. However, the *trans*-**10/3** isomer is computed to be more stable than the *cis*-**10/3** by 6.27 kcal mol^{-1} in Gibbs free energy, revealing that only the *trans*-**10/3** should be possible. This is also in line with the observed and estimated ^{31}P NMR spectrum.

Since the *cis*-**10/4** has been isolated as thermodynamically stable compound, we are interested in the stability of the expected and more stable *trans*-**10/3**. Indeed, the computed exergonic free energy (−1.48 kcal mol^{-1}) of the ligand exchange reaction (*cis*-**10/4** + **3** = *trans*-**10/3** + **4**) shows the thermodynamic possibility and stability of the expected *trans*-**10/3**.

Considering the possible *cis* and *trans* isomers of the complexes with two imidazolylphosphine ligands and two bromine atoms, we are confident that *cis*- and *trans*-isomers of the complexes should represent pre-catalysts that form in situ with molecular hydrogen the mono- or dihydrido active species for hydrogenation of nitriles.

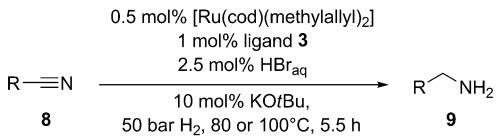
According to the scope of the catalytic hydrogenation, the influence of the alkyl chain length of nitriles was examined using 0.5 mol% $[Ru(cod)(methylallyl)_2]$/1 mol% **3** (Table 2, entries 1–5). At 80 °C, an excellent yield of propyl amine **9a** (99%, Table 2, entry 1) was achieved whilst the yields of hexyl-, heptyl- and dodecyl amine were between 66 and 77% (Table 2, entries 2–4). Increasing the temperature to 100 °C led to higher yields up to 93% (Table 2, entries 2, 3, and 5). Additionally, branched as well as cyclic nitriles can be successfully reduced at 80 or 100 °C in high yields up to 92% (Table 2, entries 7–12).

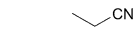
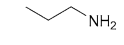
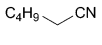
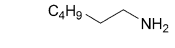
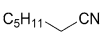
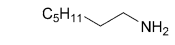
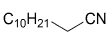
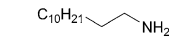
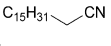
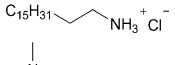
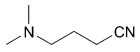
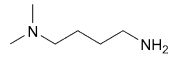
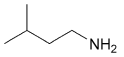
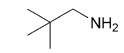
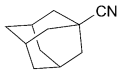
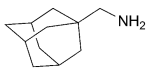
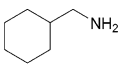
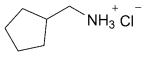
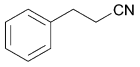
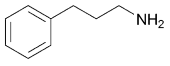
Finally, a small selection of aromatic nitriles was also hydrogenated in the presence of the related catalytic system $[Ru(cod)(methylallyl)_2]$/**1** (Scheme 3). To our delight, the corresponding primary amines are formed in almost quantitative yields already at room temperature using a low catalyst loading (0.5 mol%). Electron-donating as well as electron-withdrawing groups were accepted and gave the completely reduced products in excellent selectivity.



Scheme 3. Hydrogenation of aromatic nitriles with $[Ru(cod)(methylallyl)_2]$/**1**.

Table 2. Catalytic hydrogenation of various aliphatic nitriles—scope.[a]



	Nitrile		Amine		T [°C]	Yield [%][b]
1		**8a**		**9a**	80	99
2		**8b**		**9b**	80 100	77 93
3		**8c**		**9c**	80 100	66 67
4		**8d**		**9d**	80	77
5		**8e**		**9e**	100	86[c]
6		**8f**		**9f**	100	81
7		**8g**		**9g**	80 100	17 85
8		**8h**		**9h**	80 100	63 83
9		**8i**		**9i**	80 100	63 89
10		**8j**		**9j**	80 100	52 86
11		**8k**		**9k**	100	84[c]
12		**8l**		**9l**	80	92

[a] Reaction conditions: 5 mmol **8**, 0.05 mmol **3**, 0.025 mmol [Ru(cod)(methylallyl)$_2$], HBr_{aq} (48 wt%, 0.125 mmol), 0.5 mmol KO*t*Bu, 8 mL toluene, 50 bar H_2, 80 or 100 °C, 5.5 h. [b] Yield determined by GC methods using hexadecane as an internal standard. [c] Yield determined via isolation as HCl salt.

In summary, we have developed an efficient and effective protocol for the reduction of aliphatic and aromatic nitriles to give the corresponding primary amines in high yields. The combination of [Ru(cod)(methylallyl)$_2$] and imidazolylphosphine ligands **3** or **1** generate active homogeneous catalyst systems, which allow hydrogenation of linear, branched, and cyclic aliphatic nitriles as well as aromatic nitriles. Furthermore, we obtained two new crystal structures of ruthenium complexes **10** and **11**, which represent possible pre-catalysts for active hydrogenation catalysts.

Experimental Section

General information

Unless otherwise stated, all reactions were run under an argon atmosphere with exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds. All isolated compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy, high resolution mass spectrometry (HRMS) and HPLC. NMR spectra were recorded on Bruker AV 300. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are related to solvent peaks {[D_6]DMSO: 2.5 (^{1}H), 39.52 ppm (^{13}C) or [D_4]MeOH: 3.3 (^{1}H), 49.0 ppm (^{13}C)}. All measurements were carried out at room temperature unless otherwise stated. Mass spectra were in general recorded on a Finnigan MAT 95-XP (Thermo Electron) or on a 6210 time-of-flight LC/MS (Agilent). Gas chromatography was performed on a HP 6890 with a HP5 column (Agilent). Unless otherwise stated, commercial reagents were used without purification. All catalytic hydrogenation experiments using molecular hydrogen were carried out in a Parr Instruments autoclave (25 mL).

Hydrogenation of nitriles

Under an argon atmosphere, a Schlenk tube was charged with [Ru(cod)(methylallyl)$_2$] (0.025 mmol) and the respective ligand (0.05 mmol). After a stirring under vacuum for a short time, acetone (1 mL) and HBr_{aq} (48 wt%, 0.125 mmol) were added and the mixture was stirred again for 15 min after which a yellow-orange precipitate was formed. Afterwards, acetone was removed under vacuum and KO*t*Bu (0.5 mmol) was added. The solid was dissolved in THF (7 mL) and the liquid nitrile (5 mmol) (solid nitrile: the substrate was directly filled in the autoclave) as well as hexadecane (as standard) was added. The mixture was transferred into the autoclave and the apparatus was flushed three times with hydrogen, filled with 50 bar H_2, and stirred for 5.5 h at 80 or 100 °C. After the reaction is finished, the autoclave is cooled down to room temperature, hydrogen is released and the reaction mixture is analyzed by GC or isolated as HCl salt.

Computational methods

Structure optimizations were carried out at the BP86[11] density functional level of theory with the SVP basis set for non-metal elements (C, H, P, N, Br)[12] and the LANL2DZ basis set for Ru[13] with Gaussian 03 program package.[14] The optimized geometries are characterized as energy minimums at the potential energy surface from frequency calculations at the same level of theory (BP86/SVP); that is, energy minimum structure has only real frequencies. For the discussion and comparison of the relative stabilities single-point energies were computed at the BP86 level with the TZVP basis set for the non-metal elements.[15] The Gibbs free energies are scaled with the thermal correction to Gibbs free energies at 298 K. The computed energetic data and Cartesian coordinates are listed in Supporting Information.

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Keywords: amine · hydrogenation · nitrile · *P,N* ligands · ruthenium

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