SHORT COMMUNICATION

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Hydrogenation of Aliphatic and Aromatic Nitriles Using a Defined Ruthenium PNP Pincer Catalyst

Jacob Neumann,[a] Christoph Bornschein,[a] Haijun Jiao,[a] Kathrin Junge,[a] and Matthias Beller*[a]

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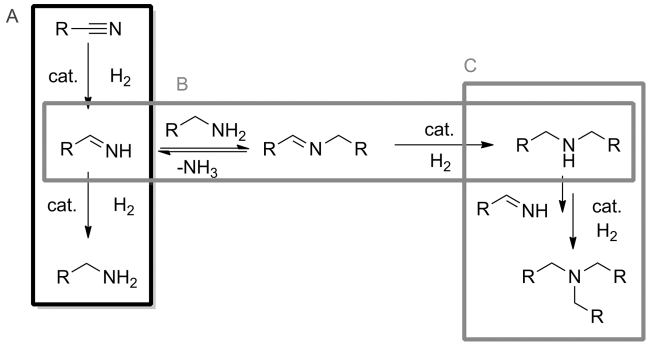
Selective catalytic reductions of nitriles are presented using the commercially available Ru-Macho-BH complex. A variety of aliphatic, aromatic and (hetero)cyclic nitriles including industrially important adipodinitrile are hydrogenated to the corresponding primary amines. Modelling suggests the reaction follows an outer sphere hydrogenation mechanism.

Introduction

Amines play an important role in our daily life and constitute key intermediates in a number of biological and chemical processes. For example, they are used as starting materials and building blocks for dyes, drugs, polymers and agrochemicals as well as for gas treatment in the chemical industry and in power plants. Hence, there exists a continuing interest in the development of novel and improved methods for the synthesis of amines. In general, catalytic reductions of nitro compounds, imines, amides or nitriles are prevailing methods for amine production. In industry, the selective production of amines from nitriles is usually realized in the presence of strongly reducing heterogeneous catalysts such as Raney® Ni or Raney® Co.[1–3] Here, often ammonia or ammonium salts are added to avoid the formation of unwanted by-products like secondary and tertiary amines.[4] In organic synthesis, on laboratory scale nitriles are typically converted into the corresponding primary amines with stoichiometric amounts of metal hydrides.[5] However, using catalysts with molecular hydrogen as reducing agent allow for a more selective, cleaner and atom-economic formation of amines.

So far, a general problem for all catalytic nitrile hydrogenation processes is the inevitable side reaction of the initially formed primary amine (A) towards the corresponding secondary imines and amines (B) as well as the tertiary amines (C) (Scheme 1).

Interestingly, the catalytic reduction of nitriles mediated by homogeneous catalysts was somewhat neglected, but recently it has attracted more and more attention by the catalytic community.[6] Until now, the homogeneous hydrogenation of nitriles to amines was realized based on Ru,[7] Ir,[8] Rh,[9] Re[10] and Mo.[11] Most of these catalytic systems make use of *P*- or *P*,*N*-ligands requiring the addition of base for catalyst activation and to prevent side reactions. Recently, also an Fe pincer catalyst developed by our group was successfully applied in various hydrogenation[12] and dehydrogenation reactions[13] including the very first iron-catalyzed nitrile hydrogenation.[12c] This iron PNP pincer complex represents an analogue of the commercially available Ru-MACHO-BH (**2**), which is well established for the reduction of esters.[14] Therefore, we became interested in the use of **2** as catalyst for the production of primary amines from nitriles. During this work another Ru pincer complex was reported by the group of Prechtl, which enabled the controlled synthesis of imines or amines from nitriles.[15]



Scheme 1. Hydrogenation of nitriles to primary amines (A) including side reactions (B) and (C).

Results and Discussion

As model reaction we investigated the hydrogenation of heptanenitrile to obtain heptane-1-amine. In the beginning, we tested different commercially available ruthenium com-

[a] Leibniz-Institut für Katalyse e.V.
Albert-Einstein-Str. 29a, 18059 Rostock, Germany
E-mail: Matthias.beller@catalysis.de
www.catalysis.de

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plexes including Ru-Macho-BH for the hydrogenation of heptanenitrile with and without base (Figure 1). In the presence of 10 mol-% of KO*t*Bu, good yield and selectivity to the corresponding heptylamine were obtained with the Ru PNP pincer complexes **1** and **2**, while Ru precursors **6**, **7** and **8** showed only moderate activity. Interestingly, without any base only Ru-Macho-BH (**2**) acted as efficient catalyst producing the primary amine in 88% yield.

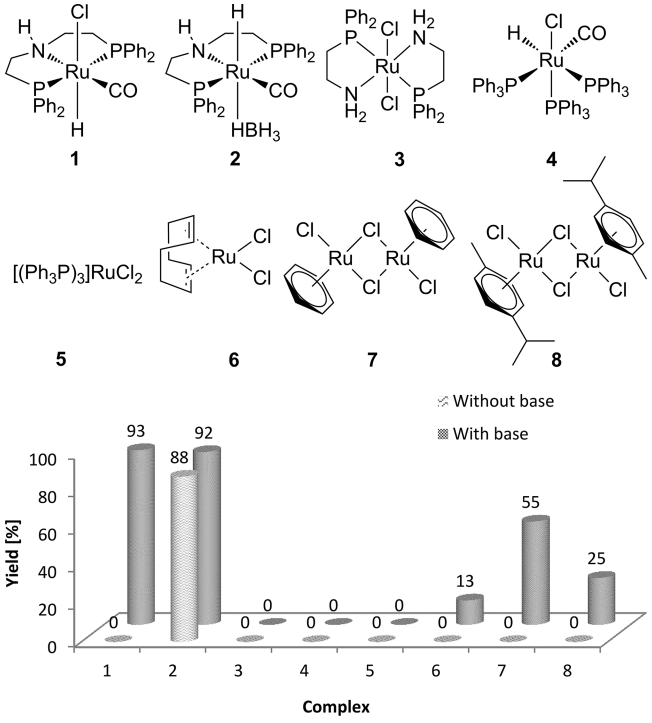
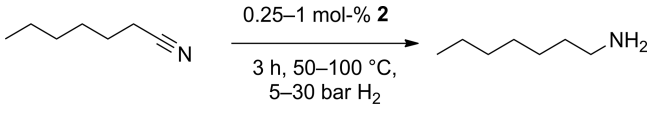


Figure 1. Observed yields for the hydrogenation of heptanenitrile by applying 1 mol-% of **1**–**8**, 2 mL of *i*PrOH, 30 bar of H_2, 70 °C, 3 h with and without the addition of 10 mol-% of KO*t*Bu.

Next, we examined the influence of different solvents, temperatures, pressure and catalyst loadings of **2** to evaluate the critical parameters, which are responsible for the formation of the desired amine (Table 1). Among the different protic and aprotic solvents investigated *i*PrOH showed the best result (Table S1). A decreased loading of the complex **2** (Table 1, Entries 2 and 3) or a reduced temperature (Table 1, Entries 4 and 5) had a significant influence on the selectivity of the nitrile reduction. Although quantitative conversion was detected, the yield of heptane-1-amine dropped down to 31%. Obviously, under these conditions the hydrogenation of the nitrile takes place by reaction pathways A and B leading to the formation of the primary and the secondary amine. However, at lower pressure heptane-1-amine is formed in good yields between 82 and 91%, and no side-reaction was observed.

To demonstrate the general applicability of the Ru-Macho-BH (**2**) catalyst for the reduction of nitriles the substrate scope was investigated under the optimized reaction conditions (1 mol-% of **2**, 30 bar of H_2, 100 °C, 3 h). As presented in Table 2, a selection of aliphatic nitriles was converted into the corresponding amines in high yields. In

Table 1. Hydrogenation of heptane nitrile catalyzed by Ru-MACHO-BH (**2**).[a]

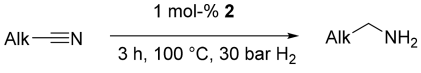


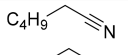
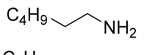
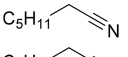
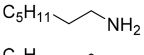
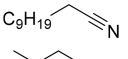
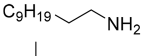
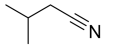
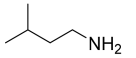
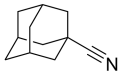
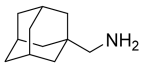
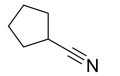
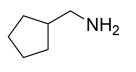
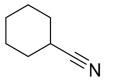
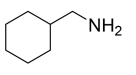
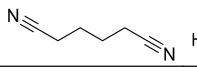
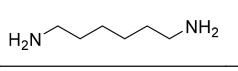
Entry	**2** [mol-%]	*T* [°C]	*p* [bar]	Conv.[b] [%]	Yield[b] [%]
1	1	100	30	> 99	94
2	0.2	100	30	> 99	71
3[c]	0.25	100	30	> 99	48
4	1	70	30	> 99	88
5[c]	1	50	30	> 99	31
6	1	100	15	> 99	91
7	1	100	5	92	82

[a] Conditions: 2.0 mmol of heptanenitrile, Ru-MACHO-BH (**2**), 2 mL of *i*PrOH, 3 h, *T*, *p*. [b] Determined by GC analysis. [c] The secondary amine was formed as side product.

general, exclusive formation of the primary amines was observed. Nevertheless, the chemoselectivity is slightly reduced with an increasing chain length of the alkyl moiety. Thus, the corresponding dodecan-1-amine is formed in 70% yield (Table 2, Entry 3). Cyclic as well as branched nitriles are converted into the primary amines with excellent selectivity and high yields (Table 1, Entries 4–7). Gratifyingly, hexane-1,6-diamine, which is used in industry for the synthesis of Nylon®, is produced in 96% isolated yield (Table 2, entry 8). It should be highlighted, that this is the first example of a homogeneous Ru-catalyzed hydrogenation of adipodinitrile.

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

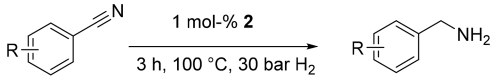


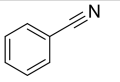
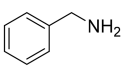
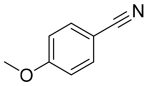
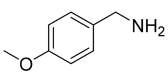
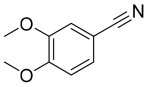
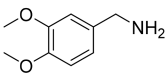
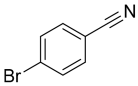
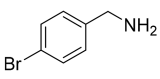
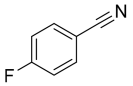
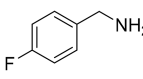
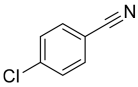
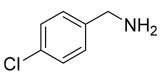
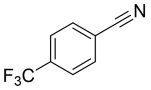
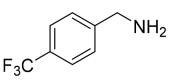
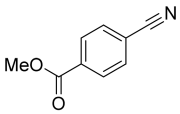
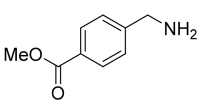
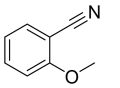
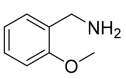
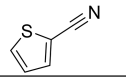
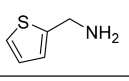
Entry	Nitrile	Amine	Conv. [%][b]	Yield [%]
1			>99	98[b]
2			>99	95[b]
3			>99	70[c]
4			>99	74[c]
5			>99	98[c]
6			>99	86[c]
7			>99	95[c]
8			>99 99	96[c] 87[d]

[a] Conditions: 1.0 mmol of nitrile, 1 mol-% of Ru-MACHO-BH (**2**), 2 mL of *i*PrOH, 30 bar of H_2, 100 °C, 3 h. [b] Determined by GC analysis. [c] Isolated yield. [d] 10 mmol of adipodinitrile, 1 mol-% of Ru-MACHO-BH (**2**), 12 mL of *i*PrOH, 30 bar of H_2, 100 °C, 3 h.

Additionally, aromatic and (hetero)aromatic nitriles were tested in the catalytic reaction (Table 3). The corresponding primary amines were isolated in good to very high yields. Functional-group tolerance was achieved for substrates containing halogen, ether or ester substituents on the aromatic ring. In case of a methoxy group in *ortho* or *para* position of the phenyl ring the product is formed in excellent yield (Table 3, Entries 2 and 3), while a substitution in *meta* position affects the efficiency of the catalyst (Table 3, Entry 9). Interestingly, the nitrile group is preferentially reduced in the presence of an ester moiety, which clearly demonstrates the chemoselectivity of the catalyst (Table 3, Entry 8). Furthermore, thiophene-2-carbonitrile was hydrogenated to the corresponding amine (Table 3, Entry 10), while furan-2-carbonitrile did not react at all. In addition, under these conditions 2-methyl-3-butenenitrile and 6-bromohexanenitrile could not successfully be hydrogenated.

Table 3. Hydrogenation of various (hetero)aromatic nitriles.[a]

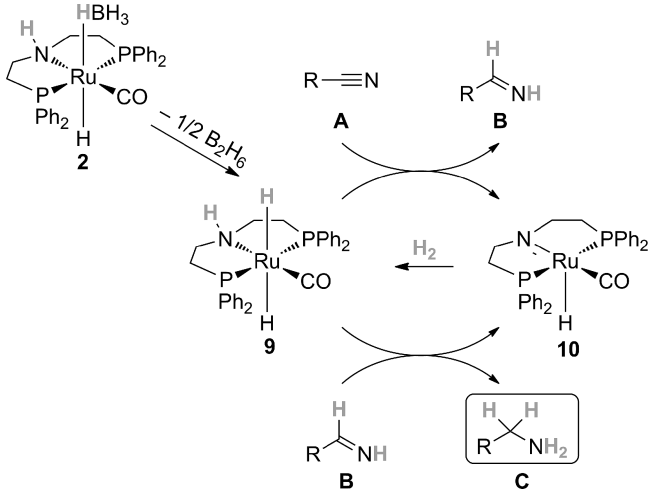


Entry	Nitrile	Amine	Conv. [%][b]	Yield [%][c]
1			>99	97
2			>99	99
3			>99	99
4			>99	98
5			>99	89
6			>99	95
7			>99	83
8			>99	94[d]
9			>99	78
10			>99	68

[a] Conditions: 1.0 mmol of nitrile, 1 mol-% of Ru-MACHO-BH (**2**), 2 mL of *i*PrOH, 30 bar of H_2, 100 °C, 3 h. [b] Determined by GC analysis. [c] Isolated yields as ammonium salt. [d] 30 bar of H_2, 130 °C, 3 h.

In order to understand the mechanism of this ruthenium-catalyzed nitrile hydrogenation, the proposed catalytic cycle has been computed. Additionally, we made a comparison to the recently disclosed related iron-catalyzed reaction, proceeding by an outer-sphere mechanism.[12c]

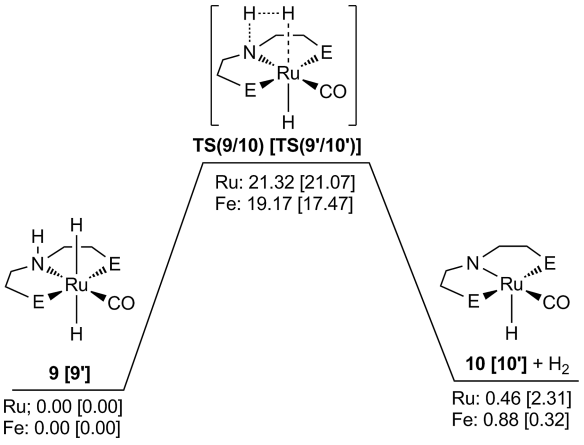
Hereby, an important feature is the reversibility between the hydrogenation and dehydrogenation of the catalyst and its amido intermediate. In our proposed mechanism in Scheme 2, the transformation of nitrile **A** into amine **C** needs two cycles via imine **B**. Firstly, the catalytically active species **9** is liberated by borane dissociation. The free dihydride complex **9** is also available from Ru-Macho (**1**) by the addition of a base as demonstrated in the initial catalytic tests (Figure 1). In the following, a simultaneous transfer of the hydride from the metal center and the proton from the nitrogen ligand of **9** takes place leading to the amido complex **10**. In the final step, intermediate **B** forms amine **C**, while **9** is regenerated by the addition of H_2 to **10**.



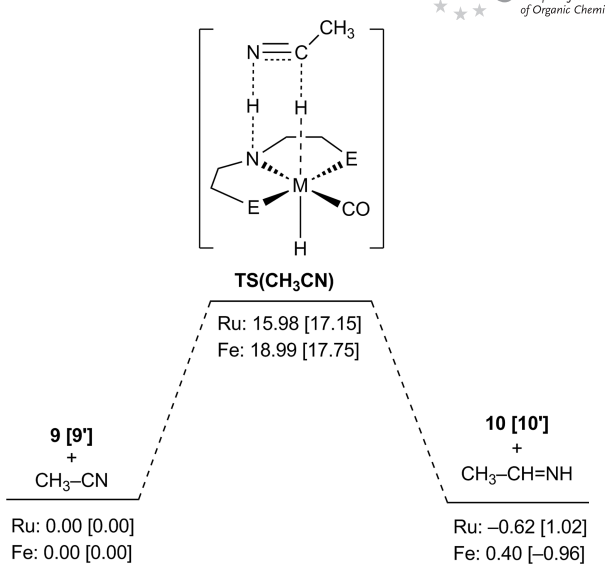
Scheme 2. Proposed mechanism for the Ru-catalyzed reduction of nitriles.

In our recent computational work,[16] we found that ruthenium complex **9′** (isopropyl instead of phenyl) should also catalyze the nitrile hydrogenation by the same outer-sphere reaction mechanism.

On the basis of the proposed mechanism in Scheme 2, we computed the acetonitrile hydrogenation by using complex **9**, and the results are compared with those of complex **9′** to show the differences caused by the substituents at the phosphorus center [phenyl (**9**/**10**) vs. isopropyl (**9′**/**10′**)]. In addition, the corresponding homologous iron pincer complex **9-Fe** is also computed for comparison. At first, we computed the equilibrium between catalyst **9** and amido intermediate **10**. As shown in Scheme 3, H_2 elimination from **9** to **10** has a free energy barrier of 21.32 kcal/mol, and the reaction is slightly endergonic by 0.46 kcal/mol, and these results are nearly the same as found for the analogous complexes (**9′** and **10′**) with the isopropyl substituent (21.07 and 2.31 kcal/mol, respectively). In addition, the free energy barriers for the back reaction are also similar (20.86 vs. 19.76 kcal/mol). This reveals the equilibrium and the reversibility under hydrogenation and dehydrogenation conditions.



Scheme 3. Potential energy surfaces [kcal/mol] for **9**/**10** inter-conversion at B3PW91 [E = $P(Ph)_2$ for **9** and **10**; E = $P(iPr)_2$ for **9′** and **10′**].



Scheme 4. Potential energy surfaces [kcal/mol] of the CH_3CN hydrogenation at B3PW91 [E = $P(Ph)_2$ for **9** and **10**; E = $P(iPr)_2$ for **9′** and **10′**].

These barriers for **9** and **10** as well as for **9′** and **10′** are higher than those (17.47 vs. 17.15 kcal/mol) of the iron complexes with isopropyl substituent, **Fe-9′** and **Fe-10′**, indicating that **Fe-9′** can be easier regenerated than **9** and **9′**. In addition, we also computed the iron complexes with phenyl substituent, **Fe-9** and **Fe-10**, and the barrier for H_2 elimination from **Fe-9** to **Fe-10** and the back reaction is 19.17 and 18.29 kcal/mol, respectively, which is lower than those for **9** and **10** as well as for **9′** and **10′**, but higher than those for **9′-Fe** and **10′-Fe** as well as for **Fe-9** and **Fe-10**.

Since the hydrogenation of imine ($CH_3CH{=}NH$) to amine ($C_2H_5NH_2$) is barrier-less by using **9′-Fe** and **10′-Fe**,[12c] we only computed the step of acetonitrile ($CH_3C{\equiv}N$) to imine for comparison. As shown in Scheme 4, the hydrogenation of acetonitrile using complex **9** has a barrier of 15.98 kcal/mol, which is lower than those using complexes **9′** (17.15 kcal/mol) as well as **Fe-9** (18.99 kcal/mol) and **Fe-9′** (17.75 kcal/mol), indicating that complex **9** is most effective.

On the basis of the barriers of the acetonitrile hydrogenation and catalyst regeneration, one can discuss the rate-determining step of the reaction. For **9** and **10**, the barrier of catalyst regeneration (20.96 kcal/mol) is higher than the barrier of acetonitrile hydrogenation (15.98 kcal/mol), and catalyst regeneration is the rate-determining step. The same is also found for **9′** and **10′** (18.76 vs. 17.15 kcal/mol). For **9** and **9′**, the barriers of the H_2 elimination are higher than those of the acetonitrile hydrogenation; **9** and **9′** are stable under hydrogenation conditions, and the reaction can take place at low H_2 pressure. For **9-Fe** and **10-Fe** as well as **9′-Fe** and **10′-Fe**, however, the catalyst regeneration has a barrier of 18.29 and 17.17 kcal/mol, respectively, which are lower than those of the acetonitrile hydrogenation (18.99 and 17.75 kcal/mol, respectively), and therefore the latter should be the rate-determining step. Since the barriers of the H_2 elimination for **9-Fe** and **9′-Fe** are similar to those of the acetonitrile hydrogenation, higher H_2 pressure is needed to enhance the stability of **9-Fe** and **9′-Fe** under hydrogenation conditions.

Conclusions

We have developed an efficient ruthenium-catalyzed protocol for the reduction of nitriles. By applying the commercially available Ru-Macho-BH complex, a variety of aliphatic, aromatic and (hetero)cyclic nitriles including the industrially important substrate adipodinitrile are selectively transformed to the corresponding primary amines. Modelling studies suggest an outer-sphere hydrogenation mechanism.

Experimental Section

General: All catalytic hydrogenation experiments using molecular hydrogen were carried out in a Parr Instruments autoclave (300 mL) under argon. Chemicals were purchased from Aldrich, Fluka and Strem and used without further purification.

Ruthenium-Catalyzed Reduction of Nitriles. General Procedure: Under argon, Ru-MACHO-BH (5.9 mg, 0.01 mmol, 1 mol-%) was charged to a 4 mL glass vial. The vial was evacuated and subsequently flushed with argon three times. Dry isopropyl alcohol (2 mL) and nitrile (1 mmol) were added to the vial. The suspension was stirred for 3 min before it was placed into the alloy plate in the autoclave. The autoclave was closed and flushed with argon for 5 min. Afterwards, the stirrer was switched on, and the autoclave was purged three times with H_2 (10 bar). Then the autoclave was pressurized with 30 bar of H_2. After 5 min, the pressure was controlled and possibly corrected. The autoclave was heated to 100 °C to start the reaction. After 3 h, the autoclave was cooled to room temperature and depressurized. The reaction mixture was analyzed by GC–MS and the isolated HCl salt by ^1H and ^{13}C NMR spectroscopy.

Isolation as HCl Salt: The reaction mixture was transferred to a 100 mL round-bottom flask, and diethyl ether (30 mL) was added. Afterwards, HCl (1 M in MeOH, 2 mL) was added to the stirred solution. The resulting precipitate was filtered and washed with diethyl ether and ethyl acetate.

Computational Details: Structure optimizations were carried out at the B3PW91[17] level of density functional theory with the TZVP[18] basis set (LANL2DZ for Ru[19]) by using the Gaussian 09 program.[20] The B3PW91 functional has been found to reasonably reproduce the results of the iron complexes with isopropyl substituent (**Fe-9′** and **Fe-10′**).[12c] The optimized geometries were characterized as energy minimums on the potential energy surface from frequency calculations at the same level; i.e., an energy minimum has only real frequencies or an authentic transition state has only one imaginary vibration mode, which connects the reactant and the product. The Gibbs free energies, which were used for discussion and comparison, were scaled with the thermal correction to Gibbs free energies at 298 K. The computed energetic data and the optimized Cartesian coordinates are listed in the Supporting Information.

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