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Authors: Tobias Schwob, Mirco Ade, and Rhett Kempe

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A Co catalyst permits the direct hydrogenative synthesis of 1*H*-perimidines from a dinitroarene and an aldehyde

T. Schwob,[a] M. Ade,[a] and Rhett Kempe*[a]

Abstract: We report here on a novel sustainable catalytic reaction: The synthesis of 1*H*-perimidines from a dinitroarene and an aldehyde in the presence of dihydrogen. We had to develop a novel earth-abundant metal catalyst permitting the efficient, highly chemoselective and consecutive hydrogenation of dinitroarenes. The catalyst is reusable and easy to handle. The use of a specific Co complex and its pyrolysis at a certain temperature is crucial to achieve high activity for the complex organic transformation. Benzylic and aliphatic aldehydes can undergo the hydrogenative condensation and many functional groups, including hydrogenation-sensitive examples such as an iodo aryl, nitrile, olefins and alkyne, can be tolerated.

The development of catalysts based on earth-abundant metals is an important area of research. Their industrial application, here mostly reusable and nanostructured catalysts are employed, could contribute to a more sustainable chemistry - specifically to the conservation of rare noble metal resources. The substitution of precious metals is especially attractive if novel selectivity patterns are observed permitting novel syntheses. Impressive progress has been achieved in the field of selective nitroarene hydrogenation employing reusable earth-abundant metal catalysts in recent years. The hydrogenation of nitroarenes is an important reaction in chemical industry since it is the method of choice for the production of aniline and its derivatives.[1] After Beller and coworkers showed that reusable catalysts based on abundantly available transition metals, such as iron[2] and cobalt[3] can mediate the chemoselective hydrogenation of nitroarenes[4], many workgroups focused on the development of catalyst systems based on non-precious metals, such as Fe,[5] Co[6] and Ni[7]. However, the direct use of nitro derivatives in more complex hydrogenative catalytic syntheses has so far been rarely disclosed. Beller and coworkers introduced the reductive amination of carbonyl compounds with nitroarenes applying cobalt-based catalyst systems,[8] while the selective synthesis of benzimidazoles and quinoxalines from amino nitroarenes was introduced by our group.[5e,9] We also reported recently on a nickel catalyst formed from a salen complex and a porous alumina support. It was shown that pyrolysis of the coordination compound led to the formation of nanoparticles embedded in a nitrogen-doped carbon layer, which had a beneficial effect on the activity and stability of the catalyst.[10] We wanted to extend this catalyst synthesis concept to other earth-abundant metals such as Co.
Herein, we report on the direct synthesis of 1*H*-perimidines from a dinitroarene and an aldehyde in the presence of a catalyst and hydrogen. Benzylic and purely aliphatic aldehydes can be employed in this novel reaction. The hydrogenative synthesis tolerates many functional groups including hydrogenation-sensitive examples (aryl iodides, nitriles and C-C double and triple bonds). Our catalyst is based on the earth-abundant metal Co, is efficient, easy to handle and its synthesis is simple and straightforward. The key to a high catalytic activity is the combination of a specific Co salen complex with commercially available charcoal. There is no direct synthesis of 1*H*-perimidines from nitroarenes and aldehydes described in the literature to the best of our knowledge. Furthermore, dinitro compounds could not be employed in any of the direct hydrogenative syntheses of aromatic *N*-heterocyclic compounds yet. Perimidines are a very important class of chemical compounds, due to their biological activity[11] and their application as ligands.[12] In addition, 1*H*-perimidines are common starting materials for the synthesis of azapyrenes, which are promising materials for the manufacturing of organic semiconductor devices.[13]

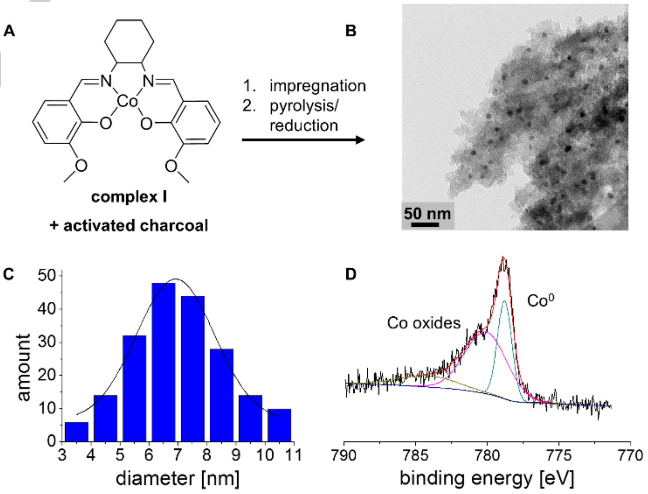

Figure 1. Catalyst synthesis and characterization. A) Synthesis of the novel catalyst by wet impregnation of commercially available charcoal with complex I, followed by pyrolysis and reduction. B) TEM analysis of the catalyst indicates homogeneously distributed Co nanoparticles. C) Size distribution of these nanoparticles with a mean diameter of 7 nm. D) XPS analysis confirms the presence of metallic cobalt and cobalt oxides or hydroxides.

Our novel catalyst (Co-Co$_x$O$_y$/C) was synthesized in a practical two-step procedure (Figure 1). At first, commercially available

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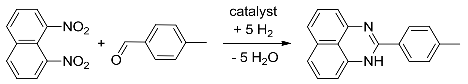
[a] T. Schwob, M. Ade, Prof. Dr. R. Kempe
Anorganische Chemie II - Katalysatordesign
Universität Bayreuth
95440 Bayreuth (Germany)
E-mail: kempe@uni-bayreuth.de

activated charcoal (Norit CA1, Cabot Corporation) was impregnated with complex I, followed by pyrolysis under a nitrogen atmosphere at 700 °C and reduction (N_2/H_2 90/10) at 550 °C (Figure 1A; for a detailed description, please see SI). The active catalyst obtains a specific surface area (Brunauer-Emmet-Teller) of 723 m^2/g and the amount of mesopores is about 40 %. This is in good accordance with the results of the pure carbon support. The hierarchical pore structure remains intact after impregnation and pyrolysis (Figure S1). Energy-dispersive X-ray spectroscopy (EDX) verifies the homogeneous distribution of the metal species over the whole carbon support indicating a clean and smooth impregnation process (Figure S2). Transmission electron microscopy (TEM) in combination with the corresponding particle size distribution provide evidence for the presence of small, homogeneously distributed Co nanoparticles with a mean diameter of 7 nm (Figure 1B,C). X-ray photoelectron spectroscopy (XPS) verifies the presence of metallic cobalt and cobalt oxides/hydroxides (Figure 1D). Inductively coupled plasma optical emission spectrometry (ICP-OES) revealed 3.5 wt% Co in the as-synthesized catalyst, which is in good agreement with the Co loading expected theoretically.

Table 1. Catalyst screening.[a]



Entry	Metal source	Pyrolysis temperature [°C]	Support	Yield [%]
1	Complex **I**	600	Activated charcoal	41
2	Complex **I**	700	Activated charcoal	72
3	Complex **I**	800	Activated charcoal	61
4	Complex **I**	700	TiO_2	31
5	Complex **I**	700	CeO_2	18
6	Complex **I**	700	γ-Al_2O_3	54
7	$Co(OAc)_2 \cdot 4\ H_2O$	700	Activated charcoal	15
8[$]	Complex **I**	700	Activated charcoal	87

[a] Reaction conditions: 0.5 mmol nitro derivative, 1.1 eq aldehyde, 35 mg catalyst (4 mol% Co), 120 °C, 6.0 MPa H_2, 3 mL toluene, 20 h; [$]130 °C reaction temperature; yields were determined by GC and GC-MS using *n*-dodecane as an internal standard. OAc = acetate.

The reductive coupling of 1,8-dinitronaphthalene and 4-methylbenzaldehyde was chosen to optimize the reaction conditions. We decided to use the nitro derivative in a technical grade, around 90 % purity, as determined by GC and GC-MS. This lowers the isolated yields of the products (Figure 2), however, the purification step of the dinitroarene can be avoided.

Varying the solvent (Table S1), the reaction temperature and the pressure, led to 87 % product formation [2-(p-tolyl)-1*H*-perimidine] in toluene at 130 °C with a hydrogen pressure of 6.0 MPa. A pyrolysis temperature of 700 °C during catalyst synthesis was found to be optimal. Pyrolysis at 600 or 800 °C led to less active catalysts (Table 1, entries 1-3). Regarding to catalyst supports, we investigated TiO_2, Al_2O_3 and CeO_2. A decrease in the product yield (Table 1, entries 4-6) was observed in all cases. The use of metal oxides as support materials led to a significant amount of aldehyde hydrogenation even at incomplete conversion of the dinitroarene derivative. This is in good agreement with the results of the Beller group, who demonstrated the hydrogenation of carbonyl compounds applying Al_2O_3- and CeO_2- based Co catalysts.[14] In addition, complex I was replaced by the common metal salt cobalt acetate, however, a significant decrease in product formation was observed (Table 1, entry 7), verifying the importance of the Co-salen complex, which had already been observed in a previous work of our group.[13] In summary, the synthesis proceeded well with a catalyst synthesized from complex I in combination with commercially available activated charcoal at a reaction temperature of 130 °C (Table 1, entry 8), 6.0 MPa hydrogen pressure applying toluene as the solvent (Table S1, entry 4). It is noteworthy to mention that it is possible to use ethanol as a more sustainable solvent when higher catalyst loadings and temperatures are applied (Figure 2, entries 4, 8, 11). With the optimized reaction conditions in hand, we were interested in the substrate scope and the functional group tolerance of our novel catalyst system. The reductive coupling of 1,8-dinitronaphthalene and benzylic aldehydes was investigated first. The introduction of methyl groups at other positions than para proceeded well, and the corresponding products were obtained in up to 84 % isolated yield (Figure 2, 2-4). To our delight, the use of halogenated substrates showed minor influence on the catalytic activity and the corresponding 1*H*-perimidines were obtained in 67-71 % yield (Figure 2, 5-9). Trace amounts of dehalogenated product were observed only in the case of 4-iodobenzaldehyde. Further aldehydes bearing functional groups, such as ethers, amides and hydroxy functionalities, were well tolerated (Figure 2, 10-13). The stability of boronic esters under reaction conditions is of special importance, since they are common starting materials for cross-coupling reactions (Figure 2, 14). The reductive coupling of 1,8-dinitronaphthalene with a heterocyclic and an aliphatic aldehyde proceeded smoothly and product yields of 75 and 85 % were observed, respectively (Figure 2, entries 17, 19). Finally, we demonstrated the possibility to introduce further reducible functionalities, such as nitriles, as well as C-C double and triple bonds. The 1*H*-perimdines desired were obtained in good to excellent yields confirming the broad applicability (Figure 2, compound 15, 16, 18, 20). The tolerance towards double bonds is especially interesting, since Chung and coworkers demonstrated the hydrogenation of olefins in the presence of carbon supported cobalt nanoparticles.[15] It is noteworthy to mention that we were able to synthesize six new products with our direct synthesis concept, starting from a technical grade 1,8-dinitronaphthalene and various benzylic and aliphatic aldehydes. The catalyst was reused in five consecutive runs to confirm its stability under reaction conditions and no remarkable decrease in catalytic activity could be detected (Figure S3). An up-scaling of the reaction (10 mmol nitro derivative) proceeded well and the 1*H*-perimidine desired was obtained in 80 % isolated yield (for a detailed description, please see SI).

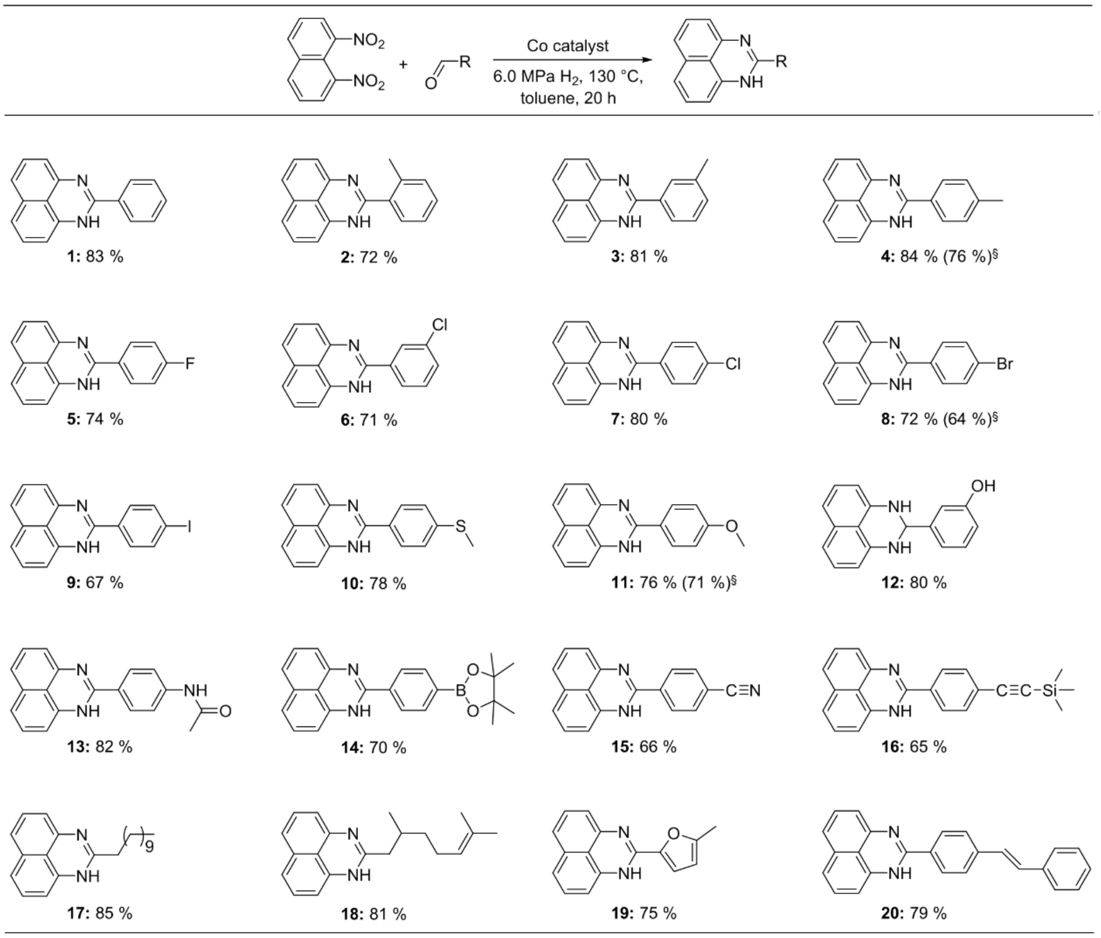


Figure 2. Highly selective synthesis of 1*H*-perimidines from 1,8-dinitronaphthalene and various aldehydes. Reaction conditions: 1.5 mmol nitro derivative, 1.1 eq. aldehyde, 120 mg catalyst (4.7 mol% Co), 130 °C, 6.0 MPa H_2, 3 mL toluene, 20 h; yields of isolated products. Note that technical grade, around 90 % purity, 1,8-dinitronaphthalene was used. Yields of isolated products were calculated assuming 100 % purity, since the purity was not uniform. §Ethanol was used as the solvent (200 mg catalyst, 7.8 mol% Co, 140 °C reaction temperature).

Mechanistically, we propose a reductive cyclization pathway via *in situ* nitroarene reduction as shown in Figure 3. The role of the catalyst is the selective and consecutive hydrogenation of the two nitro groups of the naphthalene derivative. We observed the formation of the nitro-imine intermediate as shown in Figure 3. The reaction of the hydroxylamine nucleophile, a common intermediate in the hydrogenation of nitroarenes,[16] with the electrophilic carbon of the imine is highly likely, especially under the sterically constrained conditions. This is in good agreement with the results of *Yang et al.*, who described a similar pathway for the synthesis of benzimidazoles from *o*-nitroanilines and aldehydes via reduction applying stoichiometric amounts of sodium dithionite.[17] For a further evaluation, the hydrogenation of nitrobenzene and 1-nitronaphthalene in the presence of 4-methylbenzaldehyde was investigated. In both cases, selectivity towards imine formation was observed verifying the above described hypothesis (for a detailed description, please see SI). Our catalyst cannot dehydrogenate 2,3-dihydroperimidines in toluene at 130 °C, even in an argon atmosphere, open to air via a bubble counter, assuming that a dehydrogenative pathway in the presence of 6.0 MPa hydrogen pressure is extremely unlikely. The reaction of 1,8-diaminonaphthalene with aldehydes leads to the formation of 2,3-dihydroperimidines supporting that diaminonaphthalene is not formed under reaction conditions.

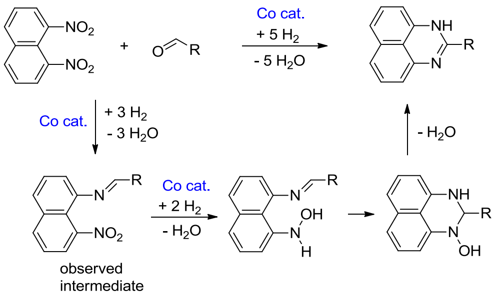


Figure 3. Proposed reaction pathway for the direct synthesis of 1*H*-perimidines via *a* nitro-imine intermediate (R = aryl or alkyl substituent).

In conclusion, a novel earth-abundant catalyst permits the first direct synthesis of 1*H*-perimidines from 1,8-dinitronaphthalene and various benzylic and aliphatic aldehydes. The catalyst is easy to synthesize by wet impregnation of commercially available charcoal with a specific cobalt salen complex, which is crucial for a high catalytic activity. Our methodology permits tolerance towards a variety of functional groups, including hydrogenation-sensitive examples (aryl iodides, nitriles, as well as C-C double and triple bonds). We synthesized six new 1*H*-perimidine derivatives and could use a technical grade dinitro derivative without purification. An up-scaling of the reaction proceeds smoothly and the catalyst shows stability over several consecutive runs without any remarkable decrease in catalytic activity. A number of challenges are associated with our novel synthesis. The key seems to be that our catalyst can selectively and consecutively hydrogenate dinitroarenes. The aldehyde must remain unaffected, even at the higher temperatures, needed for the condensation step. In addition, formation of the diaminoarene, as well as the hydrogenation of the 1*H*-perimidine have to be avoided. We think that our novel reaction represents an interesting alternative to the known literature procedures using "over-hydrogenated" 1,8-diaminonaphthalene.[18]

Experimental Section

Catalyst synthesis: To a mixture of 89 mg (M = 439.38 g mol^{-1}, 0.203 mmol) complex I and 3 mL acetonitrile, 300 mg activated charcoal were added and the suspension was stirred at 95 °C. After evaporation of the solvent, the sample was pyrolyzed under nitrogen atmosphere at 700 °C followed by reduction at 550 ° (N_2/H_2, 90/10).

Synthesis of 1-H perimidines – general procedure: A 10 mL reaction vial was charged with a magnetic stirring bar, 1.5 mmol 1,8-dinitronaphthalene, 1.1 eq. aldehyde, 3 ml toluene and 120 mg catalyst. The vial was placed in a 300 mL high-pressure autoclave (Parr Instruments) and the autoclave was flushed three times with 2.0 MPa hydrogen. Afterwards, the final pressure was applied and the reaction was stirred at 130 °C for 20 h. After completion of the reaction time, the autoclave was cooled to room temperature and the hydrogen was released. Quantitative GC analysis was accomplished using *n*-dodecane as an internal standard. For an isolation of the products, the catalyst was removed using a magnet and washed several times with acetone. The organic phases were combined and the solvent was removed under reduced pressure. Purification was accomplished by column chromatography applying pentane/ether as the eluent. The products were analyzed by NMR spectroscopy. For new compounds, elemental analysis was carried out.

Acknowledgements

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Keywords: cobalt • hydrogenation • nitroarene • perimidines

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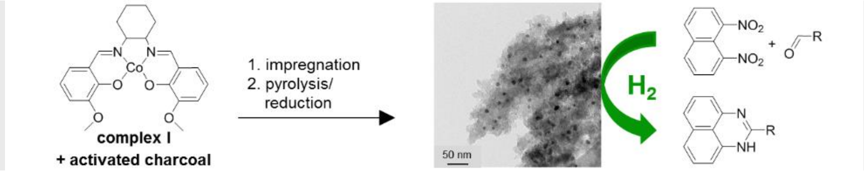

A reusable and nanostructured Co catalyst, synthesized from a specific Co complex and activated charcoal via pyrolysis, mediates the selective and consecutive hydrogenation of dinitroarenes and thus permits the direct synthesis of 1*H*-perimidines.

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A Co catalyst permits the direct hydrogenative synthesis of 1*H*-perimidines from a dinitroarene and an aldehyde