

# Liquid phase hydrogenation and hydrodenitrogenation of aromatic nitrogen-containing environmental pollutants<sup>☆</sup>

Tatiana Tehila Bovkun<sup>a</sup>, Michael Grayevsky<sup>a</sup>, Yoel Sasson<sup>b,\*</sup>, Jochanan Blum<sup>a,\*\*</sup>

<sup>a</sup> Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

<sup>b</sup> Casali Institute of Applied Chemistry, The Hebrew University, Jerusalem 91904, Israel

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## Abstract

Carcinogenic aromatic nitro-compounds are hydrogenated at 80–140 °C in the presence of a silica sol–gel entrapped combined palladium–[Rh(cod)Cl]<sub>2</sub> catalyst to give hydroaromatic amines and nitrogen-free hydrocarbons. The process involves initial transformation of the nitro to an amino function. Further hydrogenation causes denitrogenation and saturation of the aromatic moieties. Using 1-aminonaphthalene as a model substrate reveals simultaneous formation of 1- and 5-aminotetralin. While the former amine is readily converted into tetralin and 1-aminodecalins, the 5-aminotetralin gives, in a slow process, only the aminodecalins. The latter compounds are slowly denitrogenated to decalins. The catalytic hydrogenation of the aromatic compounds is accompanied by NH<sub>3</sub> elimination by which secondary amines are formed in a reversible fashion. The entrapped catalyst is leach-proof and recyclable. However, its catalytic activity in the different steps changes during the recycling. The high activity of the combined catalyst results from synergism between the two different metal nuclei.

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## 1. Introduction

Previously, we have shown that sol–gel entrapped Pd–[Rh(cod)Cl]<sub>2</sub> (**1**) [1] catalyzes the exhaustive hydrodechlorination of chloroarenes, including toxic polychlorinated-dibenzodioxines, -biphenyls, -phenoxyacetic acids and -phenols [2,3]. We have now found that this heterogenized combined catalyst also promotes the reductive detoxification of nitrogen-containing carcinogenic nitro- and amino-polycyclic aromatic hydrocarbons (see, e.g. Refs. [4,5]) under relatively mild hydrogenation conditions. Several methods for the denitrogenation of aliphatic nitro-compounds, which are based mainly on free radical operations, have been reported and reviewed [6], however, these methods are not applicable to nitro-arenes. The conventional methods for the removal of nitro functions from aromatic compounds are rather cumbersome. They require usu-

ally conversion into the corresponding amines [7] followed by deamination via diazotization or related processes [8]. In recent years, several research groups developed new methods for hydrodenitrogenation of nitrogen-containing compounds in petroleum feedstock, which are applicable also to several aromatic amines (see, e.g. Refs. [9–13]). However, these processes, which usually employ molybdenum or other transition metal compounds supported either on alumina or on related supports require high temperatures (270–400 °C). The silica sol–gel encaged Pd–[Rh(cod)Cl]<sub>2</sub> system catalyzes the stepwise hydrogenation of nitro- and amino-arenes to give hydroaromatic hydrocarbons and hydroaromatic amines already between 80 and 140 °C.

## 2. Experimental

### 2.1. Instruments

Infrared spectra were run on a Bruker model Vector 22 FTIR instrument. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 300 machine. Mass spectra were measured either on a Hewlett-Packard model 4989A mass spectrometer equipped with an

<sup>☆</sup> Dedicated to the memory of Professor Tuvia Sheradsky.

\* Corresponding author. Tel.: +972 2 6584530; fax: +972 2 6529626.

\*\* Corresponding author. Tel.: +972 2 6585329; fax: +972 2 6513832.

E-mail addresses: [ysasson@huji.ac.il](mailto:ysasson@huji.ac.il) (Y. Sasson), [jblum@chem.ch.huji.ac.il](mailto:jblum@chem.ch.huji.ac.il) (J. Blum).

HP gas chromatograph model 5890 series II or on a Q-TOF-II (Micromass, UK) spectrometer that enabled direct injection by nano-electrospray through a glass capillary at 1200 V. Gas chromatographic separations were performed on a Hewlett-Packard model Agilent, using either a 15 m long capillary column packed with bonded and crosslinked (5% phenyl)methyl polysiloxane (HP-5) or a 30 m long column packed with Carbowax 20 M-poly(ethylene glycol) in fused silica (Supelco 25301-U). The hydrogenation experiments were performed either within a glass-lined Parr microreactor model 4592 equipped with a temperature controller model 4842, a mechanical stirrer and a sampling device; or within a 45 ml Parr pressure vessel model 4712 with a gage block No. 4316.

## 2.2. Chemicals

Most commercially available starting materials and reference compounds were purchased from commercial sources. 2-Nitronaphthalene [14], *E*- and *Z*-1-aminodecahydronaphthalenes [15], *E*- and *Z*-2-aminodecahydronaphthalenes [16], 9-amino-1,2,3,4,5,6,7,8-octahydroanthracene [17], 9-amino-1,2,3,4,4a,9,10-octahydroanthracene [18], 1,2,3,4-tetrahydroanthracene [1], 1,2,3,4,5,6,7,8-octahydroanthracene [1], *Z*-1,2,3,4,4a,9,10,10a-octahydroanthracene [1], 4,5-dihdropyrene [1], 4,5,9,10-tetrahydropyrene [1], 1,2,3,3a,4,5-hexahydropyrene [1], 1,2,3,6,7,8-hexahydropyrene [1], 1,2,3,4,4a,5,5a,6,7,8-decahydropyrene [1], 1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene (one isomer) [1], 5,6-dihydrochrysene [19], 1,2,3,4-tetrahydrochrysene [19], 1,2,3,4,5,6-hexahydrochrysene [20], *E*- and *Z*-4a, 5,6,10a,11,12-hexahydrochrysene [20] and the isomeric 1,2,3,4,4a,4b,5,6,10a,11,12,12a-dodecahydrochrysene [21] were prepared according to literature procedures. The silica sol-gel entrapped Pd-[Rh(cod)Cl]<sub>2</sub> catalyst was prepared and recycled as described previously [1].

## 2.3. General procedure for the hydrotreatment experiments

Typically, the autoclave was charged under N<sub>2</sub> with the silica sol-gel entrapped catalyst **1** (prepared from 0.021 mmol [Rh(cod)Cl]<sub>2</sub>, 0.1 mmol nano-particles of palladium [1]), 2 mmol of the nitrogen-containing substrate and 5 ml of *n*-heptane. The reaction vessel was heated to the desired temperature, the N<sub>2</sub> was replaced by H<sub>2</sub> and pressurized to 27.6 bar. The reaction mixture was stirred at 150–350 rpm for the required length of time. Quantities of 20–30 μl of the liquid reaction mixture were withdrawn periodically and analyzed by GC and GC-MS. The autoclave was cooled to room temperature and unsealed. The ceramic catalyst was removed by filtration and the filtrate subjected to GC, GC-MS and NMR analyses. The data were compared with those of authentic samples. When larger quantities were used, the products were separated either on silica gel or on basic alumina. 1-Nitropyrene afforded after 14 d at 140 °C, in addition to the nitrogen-free hydrocarbons shown in Scheme 4, small amounts of 1-amino-4,5,9,10-tetrahydropyrene, 8-amino-1,2,3,3a,4,5-hexahydropyrene and a single isomer of 8-amino-

1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene that proved difficult to separate and analyze. Therefore, their structures are based only on the HRMS of their molecular peaks and their GC-MS fragmentations.

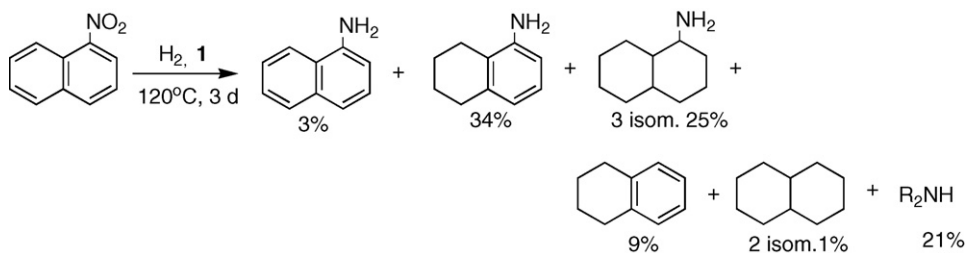
1-Amino-4,5,9,10-tetrahydropyrene: HRMS found: 221.3009. C<sub>16</sub>H<sub>15</sub>N requires 221.3015. GC-MS (70 eV), *m/z* (rel. intensity): 220 [(M-H)<sup>+</sup>, 100], 202 [(M-NH<sub>5</sub>)<sup>+</sup>, 25], 192 (C<sub>15</sub>H<sub>12</sub><sup>•+</sup>, 4). 8-Amino-1,2,3,3a,4,5-hexahydropyrene: HRMS found: 223.3155. C<sub>16</sub>H<sub>17</sub>N requires 223.3173. GC-MS (70 eV), *m/z* (rel. intensity): 222 [(M-H)<sup>+</sup>, 100], 204 [(M-NH<sub>5</sub>)<sup>+</sup>, 14], 194 (C<sub>15</sub>H<sub>14</sub><sup>•+</sup>; 31), 179 (C<sub>14</sub>H<sub>11</sub><sup>+</sup>, 21). 8-Amino-1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene: HRMS found: 227.3514. C<sub>16</sub>H<sub>21</sub>N requires 227.3489. GC-MS (70 eV), *m/z* (rel. intensity): 226 [(M-H)<sup>+</sup>, 100], 209 [(M-NH<sub>4</sub>)<sup>•+</sup>, 4], 198 (C<sub>15</sub>H<sub>18</sub><sup>•+</sup>, 17), 155 (C<sub>12</sub>H<sub>11</sub><sup>+</sup>; 10).

6-Nitrochrysene afforded after 21 d at 140 °C in addition to the nitrogen-free hydrocarbons shown in Scheme 5, 5% of 6- and 3% of 12-amino-1,2,3,4-tetrahydrochrysene. The two isomeric amines could be separated on a 15 m long HP-5 column. However, attempts to separate the two isomeric amines on preparative thin layer silica chromatography plates did not give satisfactory results. The <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) showed two multiplets of the alicyclic protons at 1.25 and 2.82 ppm. The spectrum of the 6-amino isomer showed two doublets at 8.59 (*J* = 9 Hz) and 8.62 (*J* = 8.5 Hz) that correspond to H10 and H11, respectively (the latter signal couples with that of H12 that appears at 7.65 ppm). The bay region protons of the 12-amino compound appear as a doublet at 8.78 (*J* = 7.8 Hz, H10) and as a singlet at 7.92 Hz (H11). A high field singlet at 6.57 ppm is attributed to H5 of the 6-amino-derivative. The resonance peaks of the remaining aromatic protons appear as a poorly resolvable multiplet between 7.52 and 7.82 ppm. GC-MS of the 6-amino isomer (70 eV, 20–280 °C) *m/z* (rel. intensity): 247 (M<sup>•+</sup>, 100), 230 [(M-NH<sub>3</sub>)<sup>+</sup>, 10], 219 (C<sub>18</sub>H<sub>17</sub>N<sup>•+</sup>, 13), 202 (C<sub>16</sub>H<sub>10</sub><sup>•+</sup>, 8), 191 (C<sub>14</sub>H<sub>9</sub>N<sup>•+</sup>, 11). GC-MS of the 12-amino isomer (70 eV, 20–280 °C) *m/z* (rel. intensity): 247 (M<sup>•+</sup>, 100), 230 [(M-NH<sub>3</sub>)<sup>+</sup>, 9], 219 (C<sub>18</sub>H<sub>17</sub>N<sup>•+</sup>, 16), 204 (C<sub>16</sub>H<sub>12</sub><sup>•+</sup>, 9), 191 (C<sub>14</sub>H<sub>9</sub>N<sup>•+</sup>, 8), 189 (C<sub>15</sub>H<sub>9</sub><sup>+</sup>, 8), 102 (C<sub>8</sub>H<sub>6</sub><sup>•+</sup>, 7), 56 (C<sub>4</sub>H<sub>8</sub><sup>•+</sup>, 6). mp of the mixture of isomers 120–123 °C; analysis found (of the isomeric mixture): C, 87.73; H, 6.48; N, 5.93%. C<sub>18</sub>H<sub>17</sub>N requires: C, 87.45; H, 6.88; N, 5.67%.

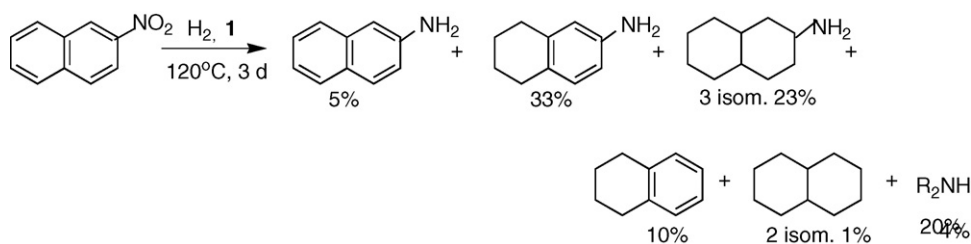
The used catalyst was washed and sonicated twice with 30 ml CH<sub>2</sub>Cl<sub>2</sub>, dried at 0.1 mm and reused in a second run.

## 3. Results and discussion

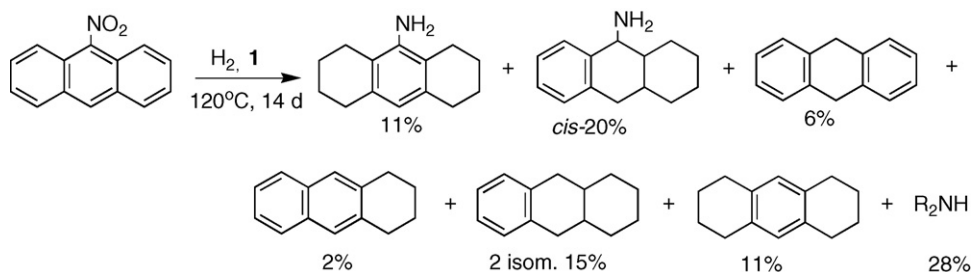
Under the conditions described in Section 2 mutagenic and carcinogenic 1- and 2-nitronaphthalene (see, e.g. Ref. [4]), 9-nitroanthracene [22], 1-nitropyrene [4,23] and 6-nitrochrysene [24] were hydrogenated. In these hydrogenations we employed the silica sol-gel entrapped Pd-[Rh(cod)Cl]<sub>2</sub> catalyst (**1**) [1] that led initially to mixtures of hydroaromatic amines and hydrocarbons, and finally after *prolonged* operation, turned into the nitrogen-free products. In Schemes 1–5 are summarized representative results. The schemes indicate that the more bulky aromatic nitro-compounds are hydrogenated much slower than the small ones and require a higher reaction temperature. While



Scheme 1.



Scheme 2.

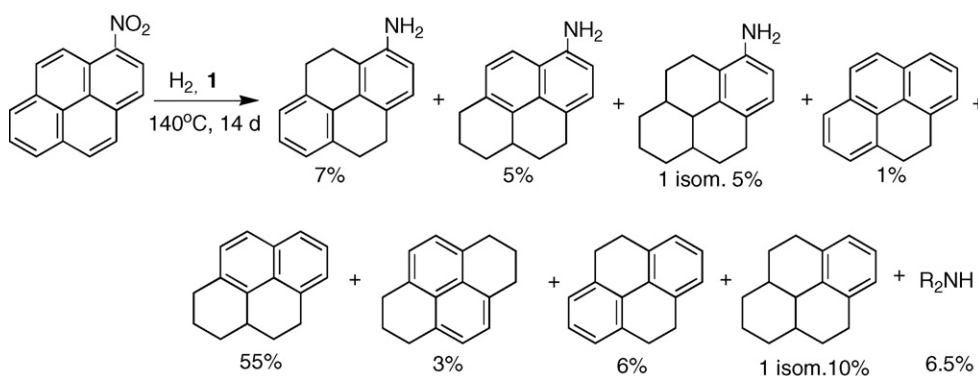


Scheme 3.

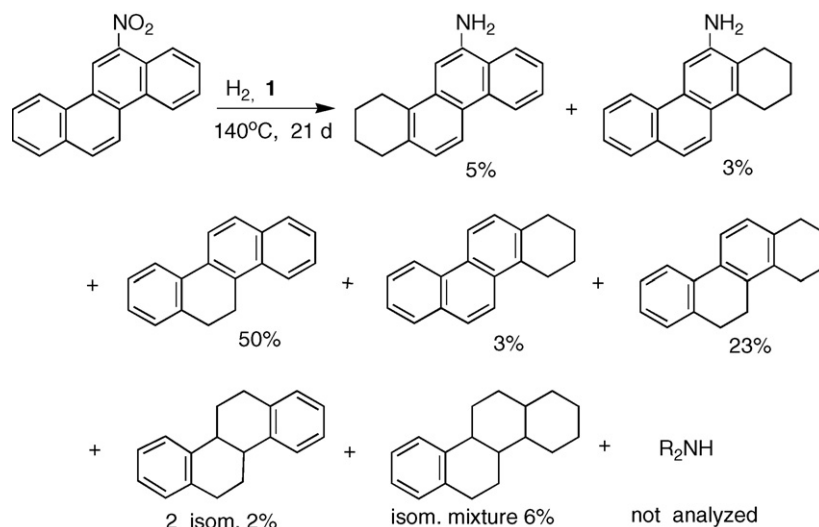
the nitronaphthalenes form decalins, in 6-nitrochrysene only one of the four aromatic rings is hydrogenated even after 21 d. This phenomenon may be associated in the first place with the limited size of the pores of the sol-gel matrix through which the substrates have to penetrate (cf., e.g. Ref. [25]).

The formation of the hydroaromatic compounds was shown to take place in several discrete steps. In all cases the first step is the conversion of the nitro group into the respective amino function by the known pathway [7]. The aromatic amines react further to give hydroaromatic amines, some of which lose ammonia to give either nitrogen-free alicyclic hydrocarbons or “dimerize” to secondary amines in a reversible process. Some of these transformations take place within a very short period

(<30 min) while others require weeks for completion. Thus, for example the transformation of 1-nitronaphthalene into nitrogen-free tetralin (26%) and isomeric decalines (71%) in the presence of **1** at 140 °C may take as long as 3 weeks. The general trend of these transformations is common to the different nitro-arenes but it is not identical. The transformations depend on the size and structural features of the substrates, on the nature of the different intermediates, on the reaction temperature and on the activity of the catalyst (*vide infra*). Although all the nitro-compounds are initially converted into aromatic amines the presence of the nitro function affects to some extent (decreases) the rates of the advanced steps in the hydrogenation process. However, it does not affect the nature of the reaction intermediates. Therefore, we



Scheme 4.



Scheme 5.

studied the main mechanistic patterns of the processes by starting with amino- rather than the nitro-compounds. As a model substrate we chose to hydrotreat 1-aminonaphthalene (**3**) [as the first transformation step of 1-nitronaphthalene (**2**)]. A typical reaction profile is shown as Fig. 1. The plots indicate transformation of 1-aminonaphthalene simultaneously to 1-amino- and 5-amino-1,2,3,4-tetrahydronaphthalene (**4** and **5**, respectively). However, while **4** is readily converted (within 25 min at 140 °C) into 1-aminodecahydronaphthalenes (**6**) together with nitrogen-free 1,2,3,4-tetrahydronaphthalene (**13**), the 5-amino isomer **5**, is transferred only to the isomers of **6** which are deaminated slowly to give ultimately (after 16 d) *E*- and *Z*-decalins (*E*- and *Z*-**14**) in a 1:3 ratio. In addition, the 1-aminonaphthalene, as well as the other amines, form secondary amines and ammonia in a reversible fashion. Thus, e.g. the 1,1'-dinaphthylamine (**7**) formed from **3** serves in fact as a feedstock of 1-aminonaphthalene and ensures its final complete conversion into nitrogen-free products. The initial fast reaction of 1-aminonaphthalene clearly follows a first order rate law until at least 95% conversion with calculated rate constant of 0.11 min<sup>-1</sup>

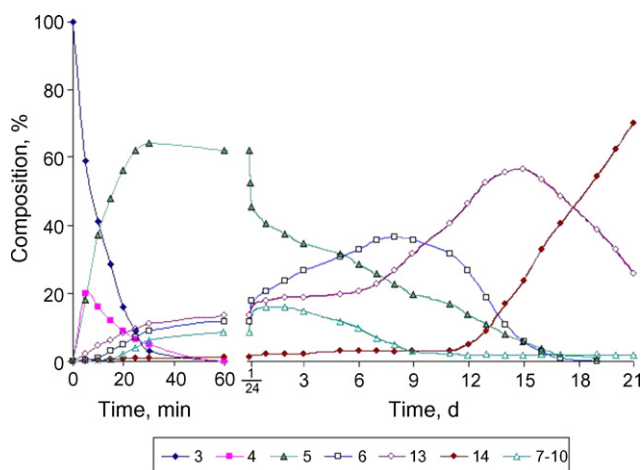


Fig. 1. Concentration time profile for the reactant and products in the catalytic hydrogenation of 1-aminonaphthalene (**3**) under the conditions of Table 1.

at 140 °C. The mass balance of the reacting system was proved as excellent with 96 mol% of the final mixture composed of **13** and **14** and the remaining 4 mol% assayed as **7–10**. In order to have further support in the assumed passway of the process, we also hydrogenated each of the individual intermediates. Some data are given in Table 1.

The products of the hydrotreatment of the 1,1'-dinaphthylamine (**7**) and of the other secondary amines proved difficult to analyze, therefore, we examined the analogous products that were formed during the hydrogenation of nitrobenzene (**15**) and aniline (**16**). At 100 °C and 27.6 bar H<sub>2</sub>, in *n*-heptane we obtained within 24 h 7% of diphenylamine (**17**), 7% phenylcyclohexylamine (**18**), 36% of dicyclohexylamine (**19**), 32% cyclohexylamine (**20**), 3% of cyclohexane (**21**) and ammonia (not analyzed quantitatively). When diphenylamine (**17**) itself was hydrogenated, we obtained, under the same conditions 7% of **16**, 9% of **18**, 57% of **19**, 7% of **20**, 3% of **21** and 13% of unreacted starting material. The amount of the monocyclic products increased when an ammonia donor was added to the hydrogenation mixture. For example, in the presence of NH<sub>4</sub>Cl ([Ph<sub>2</sub>NH]:[NH<sub>4</sub>Cl]=1:10) the reaction mixture, after 24 h, consisted of 5% **16**, 21% **18**, 31% **19**, 13% **20**, 25% **21** and only 3% of unreacted **17**.

Table 1  
Hydrogenation of 1-aminonaphthalene (**3**), and of **4–6** by sol-gel entrapped **1** at 140 °C

Starting compound	Composition of the reaction mixture after 3 d (yield, %) <sup>a</sup>				
	<b>5</b>	<b>6</b>	<b>7–10</b>	<b>13</b>	<b>14</b>
<b>3</b>	35	27	15	19	2
<b>4</b>	–	31.9	3.5	62	0.3
<b>5</b>	39	32.5	23.9	–	1.8
<b>6</b>	–	58.3	29	–	10

Reaction conditions: 2 mmol starting material; entrapped catalyst containing 0.021 mmol [Rh(cod)Cl]<sub>2</sub>; 0.1 mmol Pd; 5 ml *n*-heptane; 27.6 bar H<sub>2</sub>; 140 °C.

<sup>a</sup> The yields were determined by calibrated GC and are the average of at least two experiments that did not differ by more than ±3%.

Table 2

Effect of recycling of catalyst **1** on the distribution of the intermediates and the products during hydrogenation of 1-aminonaphthalene (**3**) at 80 °C

Run number	Composition of the reaction mixture after 3 d (yield, %) <sup>a</sup>					
	<b>3</b>	<b>5</b>	<b>6</b>	<b>7–10</b>	<b>13</b>	<b>14</b>
1	0.5	14	56	16	7	1.5
2	2	54	22	10	6.5	0.5
3	2	74	8.5	7	6.5	0.5
4	1.5	77	6	7	7	0.5
5	2	77	6	5	6.5	0.5
6	2	78	5	4.5	7	1

Reaction conditions: 2 mmol of **3**; catalyst **1** containing 0.021 mmol [Rh(cod)Cl]<sub>2</sub>; 0.1 mmol Pd; 5 ml *n*-heptane; 27.6 bar H<sub>2</sub>.<sup>a</sup> The yields were determined by GC (calibration was performed for each component) and are the average of at least two experiments that did not differ by more than ±3%.

The heterogenized Pd-[Rh(cod)Cl]<sub>2</sub> was found to be completely leach-proof (sensitivity of the atomic absorption instrument was 1 ppm) and the catalyst could be recycled in the various processes described in Schemes 1–5. However, we noticed certain changes in the ability of the recovered catalyst to promote specific steps. These changes were usually small when the catalyst was employed for relatively short reactions periods (up to 3 d) for the hydrogenation of 9-nitroanthracene, 1-nitropyrene or 6-nitrochrysene but became significant in prolonged processes. The recyclability of the catalyst was also found to depend on the temperature of the hydrotreatment. As for the transformations of 1-nitronaphthalene larger changes in the activity were observed. Some typical recycling experiments of **1** in the hydrogenation of 1-aminonaphthalene at 80 and

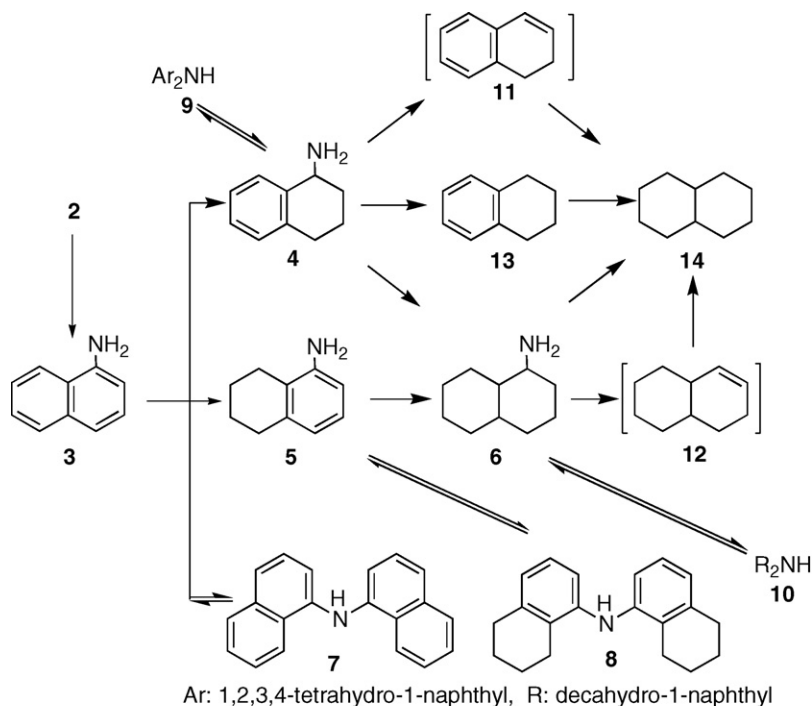
Table 3

Effect of recycling of catalyst **1** on the distribution of the intermediates and the products during hydrogenation of **3** at 140 °C

Run number	Composition of the reaction mixture after 3 d (yield, %) <sup>a</sup>				
	<b>5</b>	<b>6</b>	<b>7–10</b>	<b>13</b>	<b>14</b>
1	35	27	15	19	2
2	31	31	10	21	3
3	21	34	3	35	4
4	17	30	2	47	5

Reaction conditions: 2 mmol of **3**; catalyst **1** containing 0.021 mmol [Rh(cod)Cl]<sub>2</sub>; 0.1 mmol Pd; 5 ml *n*-heptane; 27.6 bar H<sub>2</sub>.<sup>a</sup> The yields were determined by GC (calibration was performed for each component) and are the average of at least two experiments that did not differ by more than ±3%.

140 °C after 3 d are shown in Tables 2 and 3. In these experiments hardly any starting compound was left and the mixture did not contain anymore 1-amino-1,2,3,4-tetrahydronaphthalene (**4**). At the low temperature the various compounds listed in Scheme 6 are actually formed in the first run: much of the 5-amino-1,2,3,4-tetrahydronaphthalene (**5**) is transferred to 1-aminodecahydronaphthalene (**6**). But it seems that in the following runs **1** loses gradually its ability to convert **5** to **6** and consequently, after the second run, a large amount of **5** begins to accumulate. The lack of fresh **6** also causes the decline in the formation of the secondary amine **8**. At 140 °C the amount of **6** did not vary significantly upon recycling. Moreover, it seems that at this temperature the ability of **1** to denitrogenate **3** to give tetraline (**13**) increases with time. Indeed, when we hydrogenated 1-amino-1,2,3,4-tetrahydronaphthalene (**4**) under our standard

The H<sub>2</sub> and NH<sub>3</sub> on the arrows are omitted for brevity

Scheme 6.



Table 4  
Hydrogenation of 1-aminonaphthalene by **1** and by the different components of the entrapped catalyst **1**

Catalyst system	Metal in catalyst (mmol)		Composition of the mixture after 7 d (yield, %) <sup>a</sup>					
	Pd	Rh	<b>3</b>	<b>5</b>	<b>6</b>	<b>7–10</b>	<b>13</b>	<b>14</b>
Pd-[Rh(cod)Cl] <sub>2</sub> @sol-gel	0.1	0.021	–	28	36	7	24	3
Pd@sol-gel	0.121	–	2	25	57	4	8	–
[Rh(cod)Cl] <sub>2</sub> @sol-gel	–	1.21	63	27	5	–	2	–

Reaction condition: 2 mmol of **3**; entrapped catalyst containing a total of 0.121 mmol of metals; 27.6 bar H<sub>2</sub>; 5 ml *n*-heptane; 140 °C.

<sup>a</sup> The yields were determined by GC and are the average of at least two experiments that did not differ by more than ±3%.

conditions for 1 h, we obtained with freshly prepared **1** 31.9% aminodecalins (**6**), 62% tetralin (**13**), 0.2% decalins (**14**) and 3.5% secondary amines. The application of **1** that has already promoted three previous runs, afforded 9.3% **6**, 87.8% **13**, 1.3% **14** and 1.6% secondary amines and the accumulation of **5** in advanced runs decreased (cf. also Tables 2 and 3).

As in the defunctionalization of chlorophenols [3], we showed that the hydrogenation and denitrogenation of the nitro- and amino-arenes is associated by a synergistic effect between the different metal nuclei of the catalyst. We assume that this effect resembles the one that exists in a similar immobilized Pd-Rh hydrogenation catalysts studied by Bianchini et al. [26,27]. Some comparative 1-aminonaphthalene hydrogenation experiments with **1** and with the components of **1** are shown in Table 4. The results reveal that at 140 °C the entrapped combined catalyst **1** is more efficient than either of immobilized encaged palladium or [Rh(cod)Cl]<sub>2</sub> alone.

#### 4. Conclusions

The sol-gel entrapped system of palladium nano-particles and soluble [Rh(cod)Cl]<sub>2</sub> is a powerful recyclable catalyst for the hydrodenitrogenation of some carcinogenic nitro- and aminopolycyclic aromatics under relatively mild conditions. During the hydrodenitrogenation the carcinogens are converted gradually into benign nitrogen-free hydroaromatic hydrocarbons. The catalytic activity of the heterogenized catalyst is associated with a synergistic effect between the two different metal nuclei. The individual components of the catalyst react much slower than the combined system. The hydrodenitrogenation of 1-nitronaphthalene which served as a model reaction revealed that initially the nitro group is reduced to the corresponding aromatic amine. The 1-aminonaphthalene undergoes then several parallel transformations in which two different aminotetralins are formed. One, in which the amino group is attached to the alicyclic ring loses readily ammonia to form tetralin and the second one, with an aromatic NH<sub>2</sub> moiety, is hydrodenitrogenated in an extremely slow fashion. In addition, the aminonaphthalene (as well as the other primary amino-intermediates) lose ammonia in a reversible reaction, to give secondary amines. This reversible process enables the ultimate complete denitrogenation of all nitrogen-containing intermediates to form decalins. The entire hydrodenitrogenation of 1-nitronaphthalene (or 1-aminonaphthalene) is thus characterized by the formation of five kinds of intermediates that build up significant transient concentrations. At 140 °C 1-amino-1,2,3,4-tetrahydronaphthalene

(**4**), 5-amino-1,2,3,4-tetrahydronaphthalene (**5**), the secondary amines **7–10**, the aminodecahydronaphthalenes (**6**) and 1,2,3,4-tetrahydronaphthalene (**13**), reach maximum values after 6 min, 30 min, 1 d, 8 d and 15 d, respectively.

#### Acknowledgement

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