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Selective catalytic hydrogenation of polycyclic aromatic hydrocarbons promoted by ruthenium nanoparticles†

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Ru nanoparticles stabilised by PPh_3 are efficient catalysts for hydrogenation of polycyclic aromatic hydrocarbons (PAHs) containing 2–4 rings under mild reaction conditions. These compounds were partially hydrogenated with good to excellent selectivities just by optimizing the reaction conditions. The influence of the nature of substituents present in different positions of naphthalene on the selectivity of hydrogenation was also studied. Hydrogenation of products containing substituents at position 1 is slower than that of products containing substituents at position 2. In all cases, hydrogenation takes place mainly on the less substituted ring.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) (Fig. 1) are a class of organic compounds comprising two or more fused benzene rings with different structural arrangements.[1] PAHs have attracted considerable attention due to their toxic, carcinogenic and teratogenic effects.[2] Different methods have been proposed for the elimination of PAHs such as thermal treatment, photo-degradation, chemical oxidation, *etc.*, but these processes are slow and imply complex techniques with high energy consumption.[3]

In the past few years, metal nanoparticles have been widely used in different domains such as medicine, sensors or catalysis.[4] Particularly in catalysis, nanoparticles are advantageous because of the moderate reaction conditions needed, the high activity obtained due to their high surface area, their unique electronic effects and their long lifetime.[5] Therefore, they can be attractive catalysts for PAH hydrogenation.

Stabilisation of M-NPs can be achieved by the use of polymers, surfactants or ligands, which allows the control of their size, shape and dispersion. The choice of an appropriate stabiliser for M-NPs has an important effect on their catalytic performance.[6,7]

Nanoparticles have been used in a wide range of reactions. Several studies have been focused on hydrogenation of aromatic compounds, which is an important step for the preparation of key intermediates in organic chemistry and for the production of aromatic-free-fuels.[8] In general, hydrogenation of arenes is conventionally performed with heterogeneous metallic catalysts under harsh conditions due to the stability of the aromatic rings.[9] Naphthalene has probably been the most studied polyaromatic system in hydrogenation reactions. Hydrogenation of naphthalene on some noble metals such as platinum and palladium affords decalin (decahydronaphthalene).[10] Classical Pd/C catalysts in the presence of an ionic liquid reduce naphthalene to tetralin (1,2,3,4-tetrahydronaphthalene) at 1 atm of hydrogen pressure.[11] However, hydrogenation to decalin under mild reaction conditions is still a challenge.[12] Moreover, platinum-supported catalysts were used in the reduction of naphthalene to afford decalin at 300 °C with full conversion.[13]

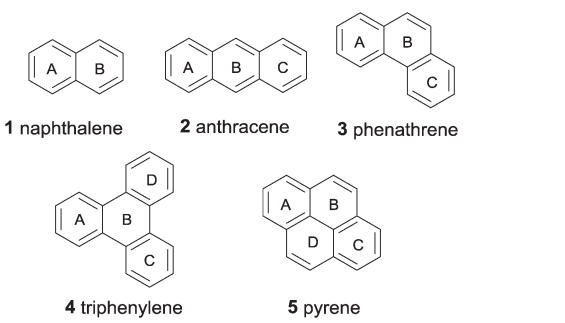

Fig. 1 PAHs of 2, 3 and 4 condensed aromatic rings studied in this work.

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Reduction of polycyclic arenes requires higher temperatures and pressures where mixtures of products are generally obtained.[14] Thus, the catalytic hydrogenation of some PAHs like naphthalene, anthracene, pyrene, *etc.* over presulfided $CoMo/Al_2O_3$ catalysts was carried out at 350 °C and 68 atm of H_2 pressure, and it was deduced that the reactivity decreased with the number of aromatic rings.[15] A palladium–rhodium system embedded in a silica sol–gel matrix was used in the hydrogenation of anthracene, phenanthrene, triphenylene, pyrene and perylene at 80 °C and 400 psi of hydrogen pressure. Mixtures of products and low selectivities were obtained in all cases.[16] For instance, in the case of anthracene, 60% of selectivity towards 1,2,3,4,5,6,7,8-octahydroanthracene was observed, in the case of phenanthrene, 37% of selectivity towards 9,10-dihydrophenanthrene was observed, or in the case of triphenylene, 27% of selectivity towards 1,2,3,4,5,6,7,8-octahydrotriphenylene was observed.

There have been only a few studies concerning the hydrogenation of PAH substrates under ambient or mild reaction conditions using nanoparticles.[17] For instance, rhodium nanoparticles were used as efficient catalysts for the hydrogenation of naphthalene affording tetralin as a unique product.[18]

In the case of polycyclic aromatic hydrocarbons with more than two fused rings, nanoparticles have also been used but totally hydrogenated products are rarely obtained.[19] Rh and Ir nanoparticles entrapped in aluminium oxyhydroxide nanofibers were tested in the hydrogenation of bicyclic and tricyclic aromatic compounds. Thus, naphthalene was reduced to tetralin and anthracene to 9,10-dihydroanthracene at room temperature and 1 bar of pressure. However, high catalyst loading (10 mol% of catalyst) was needed to achieve complete hydrogenation of anthracene.[20]

Supported Pd, Rh and Rh/Pd nanoparticle catalysts have also been used to hydrogenate anthracene showing an unusually high catalytic activity.[21] In all cases, moderate to high selectivities towards partial hydrogenation of anthracene (1,2,3,4,5,6,7,8-octahydroanthracene as the major product) were obtained; however, total hydrogenation could not be achieved even under 10 bar of H_2 pressure.

Recently, a study about the use of carbon-supported Pd nanoparticles in the hydrogenation of anthracene concluded that ring B was initially reduced to give DHA, which then isomerized to afford THA. From this intermediate, the hydrogenation progressed furnishing a fully hydrogenated compound (Scheme 1).[22]

Ruthenium nanoparticles stabilized by poly(4-vinylpyridine) were used in the hydrogenation of naphthalene, anthracene and different *N*-heteroaromatic substrates. A double mechanism for the reduction of heteroaromatic compounds which involves conventional homolytic hydrogen splitting of the simple aromatic substrates and novel heterolytic hydrogenation was proposed.[23] Naphthalene and anthracene were also hydrogenated at 150 °C and 50 bar of H_2 pressure using ruthenium nanoparticles supported on magnesium oxide. Selectivities around 80% towards the hydrogenation of one arene in naphthalene and anthracene (1,2,3,4-tetrahydroanthracene as the major product) were achieved. Furthermore, comparable selectivities towards the partial hydrogenation of N-heterocyclic compounds and selectivities up to 60% in *S*-heteroaromatics were achieved.[24]

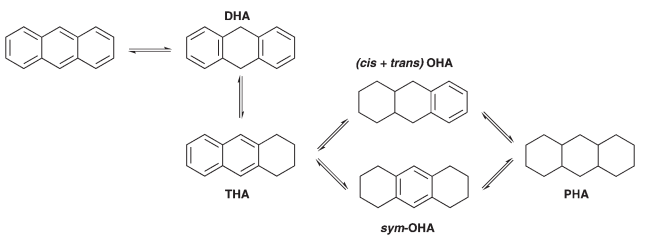
Concerning triphenylene, it is important to highlight that the central ring is very difficult to saturate.[18,25] Few examples are reported in which a totally hydrogenated product is observed.[26] With rhodium nanoparticles supported on carbon nanotubes, high selectivities towards 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene were obtained under mild reaction conditions (10 atm of H_2 and room temperature).[26b] Hydrogenation of phenanthrene and pyrene has also been attempted in the presence of supercritical carbon dioxide.[27] For instance, Pd nanoparticles stabilized by polydimethylsiloxane (PDMS) have been used to hydrogenate polycyclic aromatic hydrocarbons affording total hydrogenated products for naphthalene, anthracene, phenanthrene and pyrene (200 atm of CO_2, 10 atm of H_2).[28]

In this context, recently, we have reported the use of ruthenium and rhodium nanoparticles stabilized by PPh_3 and dppb in the hydrogenation of several aromatic ketones. Ruthenium nanoparticles stabilized by PPh_3 were found to be the most selective and active system for arene hydrogenation,[29] and we considered that these nanoparticles could also be efficient as catalysts for polyarene reduction. Here, we report that ruthenium nanoparticles stabilized by triphenylphosphine are active catalysts for the selective hydrogenation of polycyclic aromatic hydrocarbons under mild reaction conditions. A study of the effect of the nature of substituents in the selectivity of naphthalene reduction has also been performed for the first time.

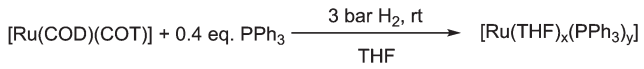
Results and discussion

Synthesis and characterization of ruthenium nanoparticles

Soluble ruthenium NPs prepared in the presence of 0.4 eq. of triphenylphosphine (Scheme 2) were synthesised by decomposition of the organometallic precursors [Ru(COD)(COT)] in THF under H_2 pressure. The NPs were isolated as black powders after precipitation with pentane and characterised by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), wide-angle X-ray scattering (WAXS), elemental analysis (EA) and thermogravimetric analysis (TGA).[29]



Scheme 1 Proposed reaction pathway for the anthracene hydrogenation using carbon-supported Pd nanoparticles as catalyst.[22]



Scheme 2 Synthesis of ruthenium nanoparticles stabilized by triphenylphosphine.

The TEM micrographs of these NPs revealed the formation of small nanoparticles with spherical shape, narrow size distribution and a diameter of *ca.* 1.3 nm. Diffuse peaks were observed in the XRD pattern of these NPs, as expected for a homogeneous distribution of very small particles with a hexagonal close-packing (hcp) lattice structure. No reflections due to ruthenium oxide were observed, and coherence lengths in agreement with TEM analysis were obtained. Thermogravimetric analysis evidenced the presence of *ca.* 2% of solvent, 30% of phosphine ligands and 70% of Ru in these nanoparticles, in agreement with previous reports in which the same nanoparticles with less proportion of ligand were used.[30]

Catalysis: hydrogenation of PAHs

Naphthalene **1** was first used to evaluate the selectivity of partial and total hydrogenation. An initial test using different solvents showed that THF was the solvent of choice to obtain better activities and selectivities in comparison to heptane, pentane or acetonitrile with which really low conversions were achieved.

When the reaction was conducted at 30 °C and 20 bar of H_2 pressure, full conversion (TON = 39) was obtained after 16 h (Table 1, entry 1). Under these conditions, total hydrogenation was achieved leading to a mixture of 84% of the product **1b** (*cis*) and 16% of the product **1c** (*trans*). When the reaction was repeated at 3 bar of H_2 pressure, quantitative conversion was observed yielding 74% of tetralin **1a**, 24% of **1b** and 2% of **1c** (Table 1, entry 2). A reduction of the reaction time to 10 h allowed the production of **1a** with an excellent selectivity (93%) and 70% of conversion (Table 1, entry 3).

Selectivities up to 97% of product **1a**[20] and 91% of product **1b**[31] in the hydrogenation of naphthalene using Rh and Pd nanoparticles and Rh nanoparticles on TiO_2 have been reported.

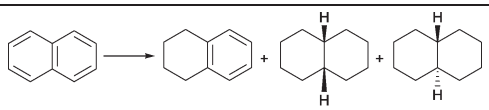
Next, the hydrogenation of polycyclic aromatic compounds containing three conjugated arenes was attempted. Initially, the optimized conditions for hydrogenation of naphthalene were tested in the hydrogenation of anthracene to afford moderate conversion (41%) and excellent selectivity of the hydrogenation of only one aromatic ring (91% of **2a**) (Table 2, entry 1). It was clear that more drastic conditions were needed in this case in order to improve the activity. Thus, when pressure was increased to 20 bar, 44% of conversion was achieved after only 0.5 hours and total selectivity towards product **2a** was observed (Table 2, entry 2). Increasing the reaction time to 9 h, full conversion and 96% of compound **2b** were obtained (Table 2, entry 3). Finally, after 16 hours, a small proportion (10%) of the completely reduced compound **2e** was detected (Table 2, entry 4).

With these results in hand and looking for additional insights into the selectivity of hydrogenation of anthracene (**2**) we studied the evolution of the reaction with time. As it can be observed in Fig. 2, full conversion was obtained after *ca.* 1 h. During the first 30 min, the conversion reached *ca.* 50% and total selectivity of the formation of product **2a** was observed, as a result of the hydrogenation of ring A of anthracene. After 40 min, product **2b** began to form progressively while the percentage of compound **2a** decreased. After *ca.* 5 hours, selectivity up to 95% of product **2b** was achieved. Only traces of products **2c** and **2d** were detected during the reaction (maximum of 5%). Product **2e** was progressively formed reaching 10% after 16 h.

Comparing these results using Ru NPs with those reported using Pd catalytic systems[22] suggests a difference in the hydrogenation mechanisms. With palladium, reduction of ring B to give compound **2d** is initially observed (Scheme 2), while with ruthenium catalysts, ring A is clearly reduced first and only traces of compound **2d** are observed along the reaction. This can suggest that in the case of ruthenium, the reaction proceeds under kinetic control, which is probably determined by the accessibility of the arene to the nanoparticle surface. This can also suggest a different hydrogen transfer mechanism in the case of palladium.

Aiming to compare the reactivity of the different polyarenes, the same reaction conditions (20 bar of H_2, 30 °C and 16 hours) were applied to the hydrogenation of phenanthrene

Table 1 Hydrogenation of naphthalene **1** catalysed by ruthenium NPs[a]

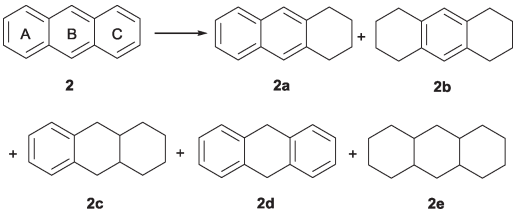


1 **1a** **1b** **1c**

E.	*P* (bar)	Time (h)	Conv.[b] (%)	TON[c]	%**1a**[b]	%**1b**[b]	%**1c**[b]
1	20	16	100	39	—	84	16
2	3	16	100	39	74	24	2
3	3	10	70	27	93	7	—

[a] General conditions: Ru-NPs (2 mol%), substrate (0.62 mmol), THF (10 ml), T = 30 °C. [b] Determined by GC. [c] TON was defined as the number of moles of the substrate converted per mole of surface Ru.

Table 2 Hydrogenation of anthracene **2** using Ru nanoparticles[a]



E.	*P* (bar)	Time (h)	Conv.[b] (%)	TON[c]	%2a[b]	%2b[b]	%2c[b]	%2d[b]	%2e[b]
1	3	16	41	16	91	6	—	3	—
2	20	0.5	44	17	100	—	—	—	—
3	20	9	100	39	—	96	1	—	3
4	20	16	100	39	—	90	—	—	10

[a] General conditions: Ru-NPs (2 mol%), substrate (0.62 mmol), THF (10 ml), T = 30 °C. [b] Determined by GC. [c] TON was defined as the number of moles of the substrate converted per mole of surface Ru.

3 but the obtained conversion was only 6%. Products **3b–c**, resulting from reduction of terminal rings A and C, were obtained with 58% selectivity, while 42% of the product **3a**, resulting from the reduction of ring B, was obtained in this case (Scheme 3). Increasing the temperature to 50 °C slightly improved the conversion to 24% but the selectivities towards **3b–c**/**3a** remained unchanged.

Despite having the same number of fused benzene rings, the behaviour of anthracene (**2**) and phenanthrene (**3**) towards hydrogenation with Ru nanoparticles is really different. TON values in the hydrogenation of phenanthrene (**3**) are much lower but in both substrates the reduction of terminal rings A and C is preferred compared to the reduction of ring B. The low selectivity observed in the reduction of phenanthrene is in agreement with previous results dealing with the reduction of this substrate catalysed by Rh nanoparticles and by Mo and Fe catalysts.[18,32] It seems that interaction of the phenanthrene with the surface of the nanoparticle is more hindered than that of the anthracene. However, the relative rate of reduction of ring B is higher than that in the case of anthracene in which compound **2d** is only observed as traces. This most probably results from the possibility of coordinating the accessible double bond of this B-ring exposed to Ru atoms of the nanoparticle. It is worth noting that good selectivities (~70%) towards compound **3a** have been reported using heterogeneous catalyst such as PtO_2 (ref. 33) or niobium.[34]

Then, hydrogenation of compounds containing four fused rings such as triphenylene **4** and pyrene **5** was studied. Initially, triphenylene **4** was hydrogenated under the optimized reaction conditions (20 bar of H_2 and 30 °C) and after 16 hours a conversion of 61% was achieved. Product **4a** which has only one arene hydrogenated was obtained with a selectivity of 53%, product **4b** (2 external rings hydrogenated) with a selectivity of 12%, and product **4c** (3 external rings hydrogenated) with a selectivity of 35% (Table 3, Entry 1). An increase in temperature to 80 °C allowed full conversion of **4** and exclusive formation of product **4c** (Table 3, entry 2). Under the conditions tested, the fully hydrogenated product was not observed. Increasing the reaction time to 60 hours, only traces of the fully hydrogenated product **4e** were detected (Table 3, entry 3). It is interesting to note that 10% of product **4d** containing one double bond bridging two arene rings was observed. This double bond is of course the most difficult to hydrogenate.

The hydrogenation of triphenylene **4** was monitored by GC-MS (Fig. 3) to look for information about the selectivity of the formation of compounds **4a–c**. All of these 3 products were detected soon after the beginning of the reaction. After 2 h, conversion reached *ca.* 20% and selectivity towards product **4a** was 70%. Then, the percentage of **4a** started to decrease and product **4c**, with three hydrogenated external arenes, started to form progressively in a major proportion. The percentage of product **4b** was practically maintained

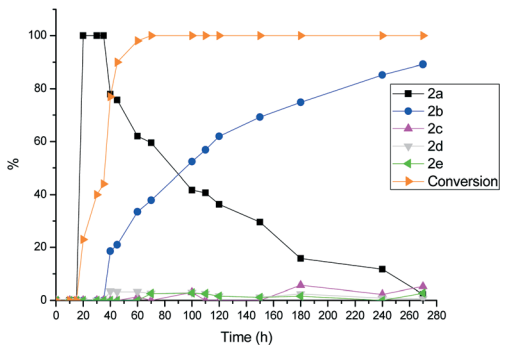
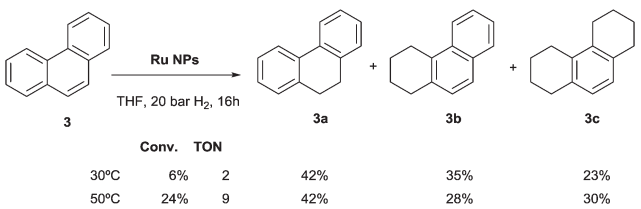
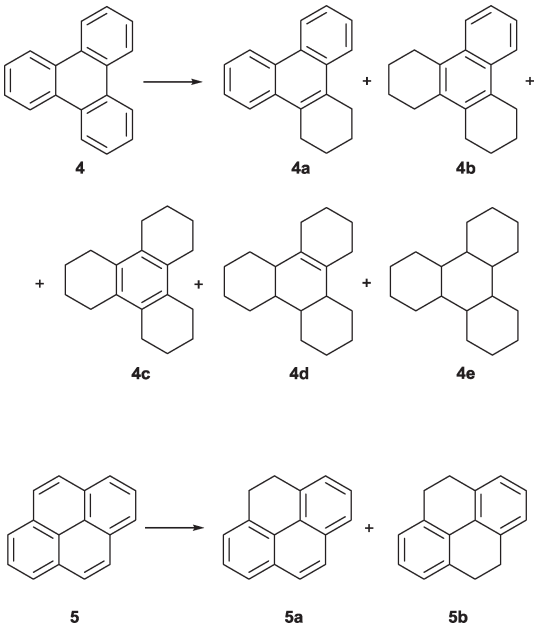


Fig. 2 Monitoring of the catalytic hydrogenation of anthracene (**2**). Conditions: Ru-NPs (2 mol%), substrate (0.62 mmol), solvent = THF, T = 30 °C, P = 20 bar of H_2).



Scheme 3 Hydrogenation of phenanthrene **3**.

Table 3 Hydrogenation of triphenylene **4** and pyrene **5**[a]



E.	Subs.	*P* (bar)	*T* (°C)	Time (h)	Conv.[b] (%)	TON[c]	%a[b]	%b[b]	%c[b]	%d[b]	%e[b]
1	**4**	20	30	16	61	24	53	12	35	—	—
2	**4**	20	80	16	100	39	—	—	100	—	—
3	**4**	20	80	60	100	39	—	—	88	10	1
4	**5**	20	50	16	17	7	93	7	—	—	—
5	**5**	20	80	16	25	10	90	10	—	—	—
6	**5**	20	80	60	44	17	86	14	—	—	—

[a] General conditions: Ru-NPs (2 mol%), substrate (0.62 mmol), THF (10 ml). [b] Determined by GC. [c] TON was defined as the number of moles of the substrate converted per mole of surface Ru.

during the reaction. The fully hydrogenated product was not observed showing, as previously commented, the difficulty in reducing product **4c**.

Pyrene **5** is much less reactive. Thus, when the reaction was performed at 50 °C and 20 bar of pressure (Table 3, entry 4), only 17% of conversion was obtained but selectivity towards product **5a** was 93%. Increasing the temperature to 80 °C, the conversion slightly increased to 25% without a substantial change in the selectivity (Table 3, entry 5) and when the reaction was left for 60 hours, the conversion increased to 44% and the selectivity towards product **5a** remained high (86%) (Table 3, entry 6).

The results reported show that reactivity decreases when the number of condensed aromatic rings increases. For that reason, harsher reaction conditions are needed to obtain moderate conversions in compounds containing several fused rings. Concerning the selectivity, in the case of triphenylene **4**, compound **4c** can be exclusively obtained, in agreement with the reported results using Rh and Pt nanoparticles.[26a] Nevertheless, compound **4a** can be obtained in ~50% of selectivity with 61% of conversion, which is the highest selectivity reported for this compound with similar conversion.

In the case of pyrene, excellent selectivities towards product **5a** were detected at moderate conversions. Different publications have been focused on hydrogenation of pyrene obtaining mixtures of products and high temperatures were required in order to obtain good conversions.[16,18] Using Pt nanoparticles supported on carbon nanotubes, total selectivity towards product **5a** was achieved but the best conversion was only 7%.[26a]

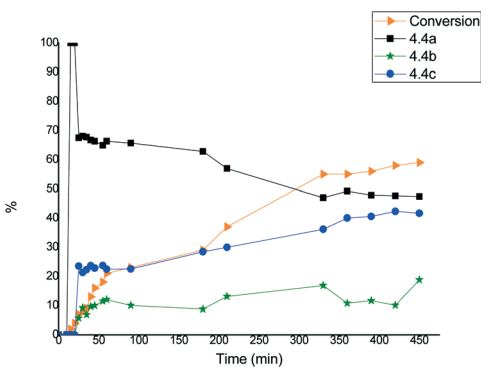


Fig. 3 Monitoring of the catalytic hydrogenation of triphenylene (**4**). Conditions: Ru-NPs (2 mol%), substrate (0.62 mmol), solvent = THF, *T* = 30 °C, *P* = 20 bar of H_2).

The results obtained in the hydrogenation of PAHs **1–5** show that high selectivities towards different partially hydrogenated products can be obtained in all cases except for phenanthrene (**3**), and forcing the reaction conditions or increasing the reaction time, fully hydrogenated products can also be obtained in some of the substrates, namely, naphthalene (**1**) and anthracene (**2**).

As discussed above, the catalytic hydrogenation of naphthalene has been the most studied system among PAHs. However, to the best of our knowledge, there are no studies dealing with the influence of ring substituents on the selectivity of arene reduction. We have shown that good results in terms of activity and selectivity can be obtained in the reduction of naphthalene using ruthenium nanoparticles (Table 1). For this reason, it was considered interesting to study substitution effects on a naphthalenic system, considering the nature of the substituent and the position.

Catalysis: hydrogenation of substituted naphthalenes *vs.* other functionalities

As mentioned above, few examples are reported to be related to the effect of substitution on the selectivity of polyarene hydrogenation, as well as to the selective reduction of polyarenes *vs.* other functional groups.[35] In order to gain information about these two aspects, reduction of substituted naphthalenes was studied. Different substitutions were considered, namely, substitution at positions α (position 1) and β (position 2), donor and acceptor substituents, and substituents that could be competitively reduced.

Initially, 2-methoxynaphthalene **6** was used as a model substrate. When the reaction was performed in THF at 30 °C, 20 bar for 2.5 hours, a conversion of 31% and a selectivity of 83% in compound **6a** were obtained (Table 4, entry 1). Hydrogenation of the less substituted ring was mainly produced. The reaction was also carried out in pentane and ethanol leading to excellent selectivities (up to 93%) towards product **6a** although conversions were low (Table 4, entries 2 and 3). Interestingly, when MTBE was used as solvent (Table 4, entry 4), conversion up to 35% and a selectivity of 91% towards **6a** were obtained. In order to increase the conversion, the reaction was performed for 16 h but the conversion was still moderate (52%) and the selectivities were comparable to the ones obtained using THF as solvent (Table 4, entry 5).

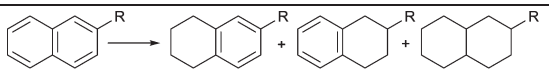
When the reaction was performed in a lower substrate/catalyst ratio (0.62 mmol of the substrate) with MTBE as the solvent, the selectivity was still good (81%) and the conversion increased to 100% (Table 4, entry 6). Driving the reaction in THF under similar reaction conditions (Table 4, entry 7), the selectivity towards **6a** remained unchanged (83%) but the conversion reached 91% within only 2.5 hours (6 times shorter than using MTBE). From these assays THF was selected as the solvent.

Next, we reduced the pressure aiming at enhancing the selectivity. When the reaction was performed under 10 bar of H_2 for 2.5 hours, the selectivity was found similar but the conversion dropped to 11% (Table 4, entry 8).

Unexpectedly, when substrate **7** containing a methyl group instead of a methoxy group was hydrogenated, a very low conversion (6%) was achieved after 16 h, although the selectivity (79%) towards product **7a** was similar to that obtained in the previous examples (Table 4, entry 9). Moreover, when substrate **8** containing an ester group was hydrogenated, no conversion was obtained indicating that, in the presence of an electron-withdrawing group, the reaction slowed down (Table 4, entry 10).

In conclusion, the introduction of substituents at position 2 of naphthalene slows down the reaction compared with that of unsubstituted naphthalene, and the reduction preferably takes place on the non-substituted ring. The observed selectivity cannot be strictly related to the donor or acceptor abilities of the substituents, since when a weak donor

Table 4 Hydrogenation of 2-substituted naphthalenes[a]



6 R=OMe, **7** R=Me, **8** R=$COOCH_3$ | **6a** R=OMe, **7a** R=Me, **8a** R=$COOCH_3$ | **6b** R=OMe, **7b** R=Me, **8b** R=$COOCH_3$ | **6c** R=OMe, **7c** R=Me, **8c** R=$COOCH_3$

E.	Subs.	Amount (mmol)	Solvent (ml)	*P* (bar)	Time (h)	Conv.[b] (%)	TON[c]	%**a**[b]	%**b**[b]	%**c**[b]
1	6	1.24	THF (10)	20	2.5	31	24	83	11	6
2	6	1.24	Pentane (10)	20	2.5	14	11	93	3	4
3	6	1.24	EtOH (10)	20	2.5	18	14	91	6	3
4	6	1.24	MTBE (10)	20	2.5	35	27	91	5	4
5	6	1.24	MTBE (10)	20	16	52	20	89	6	5
6	6	0.62	MTBE (10)	20	16	100	39	81	6	13
7	6	0.62	THF (10)	20	2.5	91	35	83	11	6
8	6	0.62	THF (10)	10	2.5	11	4	83	12	5
9	7	0.62	THF (10)	20	16	6	2	79	14	7
10	8	0.62	THF (10)	20	16	0	0	—	—	—

[a] General conditions: Ru-NPs (2 mol%), T = 30 °C. [b] Determined by GC. [c] TON was defined as the number of moles of the substrate converted per mole of surface Ru.

substituent such as Me is present, conversion is really low, as well as when there is an acceptor group such as an ester. A possible explanation can be related to the coordination of the heteroatoms with the nanoparticle surface. Thus, while the oxygen of the substituted arene in **6** may interact with the metal surface upon approaching the nanoparticle, this interaction through the carbonyl group in the case of the ester function of **8** will probably leave the arene far away from the surface which could explain the lack of reactivity. The methyl group will only provide a steric hindrance as the arene approaches the surface.

The study was continued by reducing naphthalenes containing a substituent in position 1 (Table 5). When substrate **9** containing a methoxy group was reduced under standard conditions (Table 5, entry 1), 85% of product **9a** was obtained with 40% of conversion. Running the reaction for 16 hours allowed full conversion but the selectivity was shifted towards product *cis*-**9c** (65%) (Table 5, entry 2). Curiously, no product **9b** was observed in this case.

Interestingly, when an electron withdrawing group like $-CF_3$ is present in position 1 (substrate **10**), the selectivity of the hydrogenation of the more substituted arene relatively increases leading to compound **10b** with 31% selectivity at moderate conversion (Table 5, entry 4). Changing the solvent to MTBE (Table 5, entry 5), the conversion decreased to 15% although the selectivity towards product **10a** increased to 85%.

Finally, substrate **11** containing an amine group was reduced for 16 h at 20 bar leading to a conversion of only 16% (Table 5, entry 6). Despite the long reaction time, total selectivity towards product **11a** was detected, indicating that only the unsubstituted arene ring was reduced.

In conclusion, the selectivity is affected when an electron donating group or an electron withdrawing group is present. The presence of an electron-withdrawing group slightly favours the reduction of the more substituted ring. When an amine group is present in the substrate (**11**), the conversion decreases considerably, even after several hours of reaction. This result is in agreement with those reported in the bibliography.[36]

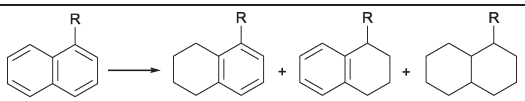
By comparing Tables 4 and 5, it can be deduced that the position of the substituent has more influence on the conversion than on the selectivity. When the substituent is at position 1, conversions are lower probably due to the higher steric hindrance and the consequent difficulty for the substrate to approach the nanoparticle surface. Nonetheless, the selectivity is not significantly affected and the arene which does not contain substituents is also preferably hydrogenated. These results agree with the necessity for the arene ring to approach and coordinate with the nanoparticle's surface in order to be reduced.

Hydrogenation of naphthalenes containing ketones was then studied (Tables 6 and 7). As expected, when a ketone is present in the substrate, there is competition between the reduction of the arene and the reduction of the ketone.[29,37]

Initially we studied the hydrogenation of compound **12**, which has an acetyl group located at position 2, under standard reaction conditions leading to full conversion in 2.5 h (Table 6, entry 1). Three products, **12a–12c**, resulting from the reduction of the less substituted ring (**12a**), the keto group (**12b**) and both the less substituted group and the keto group (**12c**) were obtained. The presence of a methyl group at position 6 in compound **13** placed both rings with the same substitution pattern. The increase in substitution in **13** results in a decrease in conversion and hydrogenation of the A ring, and hence a preferred reduction of the keto group (Table 6, entry 2). In this case, full reduction of the aromatic rings was not achieved.

Next, we studied the hydrogenation under standard conditions of compound **14**, in which the acetyl group is situated in position 1. Full conversion was observed and a complex mixture was produced (Table 7, entry 1). The previous observation that the substitution at position 1 has a negative effect on the arene reduction translates in this case into a higher relative percentage of ketone reduction, compared with compound **12**. However, it is also worth noting that small percentages of product **14e** resulting from the reduction of the more substituted ring (B), or the presence of fully reduced product **14f**, were observed. These facts indicate that the

Table 5 Hydrogenation of 1-substituted naphthalenes[a]



9 R=OMe
10 R=CF_3
11 R=NH_2

9a R=OMe
10a R=CF_3
11a R=NH_2

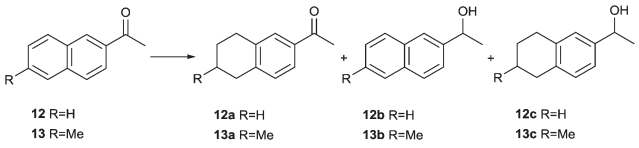
9b R=OMe
10b R=CF_3
11b R=NH_2

9c R=OMe
10c R=CF_3
11c R=NH_2

E.	Subs.	Amount (mmol)	Solvent (ml)	Time (h)	Conv.[b] (%)	TON[c]	%a[b]	%b[b]	%c[b]
1	9	0.62	THF (10)	2.5	40	15	85	11	4
2	9	0.62	THF (10)	16	100	39	35	—	65
3	10	0.62	THF (10)	2.5	45	17	63	31	6
4	10	0.62	MTBE (10)	2.5	15	6	85	15	—
5	11	0.62	THF (10)	16	16	6	100	—	—

[a] General conditions: Ru-NPs (2 mol%), P = 20 bar of H_2, T = 30 °C. [b] Determined by GC. [c] TON was defined as the number of moles of the substrate converted per mole of surface Ru.

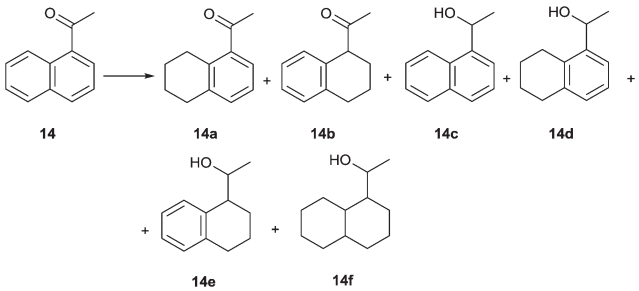
Table 6 Hydrogenation of 2-ketonaphthalenes with Ru-NPs[a]



E.	Subs.	Time (h)	Conv.[b] (%)	TON[c]	%a[b]	%b[b]	%c[b]
1	12	2.5	100	39	52	26	23
2	13	2.5	44	17	16	84	—

[a] General conditions: Ru-NPs (2 mol%), substrate (0.62 mmol), P = 20 bar of H_2, T = 30 °C. [b] Determined by GC. [c] TON was defined as the number of moles of the substrate converted per mole of surface Ru.

Table 7 Hydrogenation of 1-acetonaphthone with Ru-NPs[a]



E.	P (bar)	Time (h)	Conv.[b] (%)	TON[c]	%a[b]	%b[b]	%c[b]	%d[b]	%e[b]	%f[b]
1	20	2.5	100	39	38	—	24	25	9	4
2	10	16	100	39	24	8	8	36	14	10

[a] General conditions: Ru-NPs (2 mol%), substrate (0.62 mmol), P = 20 bar of H_2, T = 30 °C. [b] Determined by GC. [c] TON was defined as the number of moles of the substrate converted per mole of surface Ru.

presence of the keto group at position 1 of ring B increases the hydrogenation ability of this ring.

This fact was confirmed upon carrying out the reaction at 10 bar of hydrogen pressure. After 16 hours of reaction, a similar mixture of products was observed. However, now even the products **14b**, **e** resulting from the exclusive hydrogenation of ring B, which was the more substituted one, were detected (Table 7, entry 2).

From the results observed in Tables 6 and 7, it can be concluded that reduction involves important competition between the arene and the ketone groups and it is influenced by the position of the keto group. Thus, when the keto group is at position 2 (**12**) reduction of the less substituted aromatic ring takes place principally, although significant reduction of the carbonyl group is also observed. If the keto group is at position 1 (**14**), the most relevant observation is the fact that the most substituted ring is also reduced. The fact that electron-withdrawing groups activate the hydrogenation of the neighbouring ring was already observed in the case of a trifluoromethyl derivative, compound **10**.

Conclusions

In conclusion, ruthenium nanoparticles stabilized by triphenylphosphine are good catalysts for hydrogenation of PAHs under mild conditions leading to good activities and selectivities. In general, the reaction rate decreases when the number of aromatic rings increases. The disposition of the rings has also an influence on the reaction rate and, for instance, phenanthrene reacts much slower than anthracene which is in agreement with its greater difficulty in approaching the nanoparticle's surface.

The main results of conversion and selectivity are presented in Fig. 4 and can be summarized as follows: a) naphthalene is hydrogenated to tetralin (**1a**) or decalin (**1b**), *cis*/*trans* = 84 : 16, just by adjusting the hydrogen pressure. b) Anthracene can be selectively hydrogenated to compound **2a** (hydrogenation of one external ring) with total selectivity and 44% conversion, or to compound **2b** (hydrogenation of both external rings) with 96% selectivity and full conversion. c) Triphenylene has 3 equivalent rings and partial selectivity of hydrogenation is difficult to achieve. Thus, compound **4a** (hydrogenation of one external ring) can be obtained with a selectivity of 53% and a conversion of 61%, which in spite of being quite low is one of the best reported in the bibliography. The selective reduction of the 3 external rings to give compound **4c** was achieved with 100% selectivity and full conversion. d) Pyrene and phenanthrene were difficult to hydrogenate and 88% of selectivity toward compound **5a** was obtained with 44% conversion. e) Complete hydrogenation

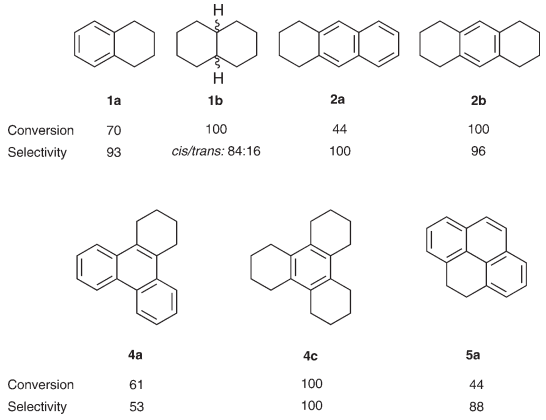


Fig. 4 Main results of conversion and selectivity of PAH reduction with Ru/PPh_3 NPs.

studied under mild conditions was only achieved for naphthalene; in the case of anthracene small amounts of the fully reduced product were detected. f) There are only a few mechanisms proposed for PAH hydrogenation. In general, we have observed that there is competition between kinetic and thermodynamic control, which affects the reduction of the less substituted ring *versus* preservation of aromaticity. Compare for instance compounds **2** and **3**.

From the study of the chemoselective reduction of substituted naphthalenes, the following conclusions can be extracted: a) substitution has an important effect on reactivity and selectivity. Reactions are slower in substituted naphthalenes, and hydrogenation principally takes place in the ring that does not contain substituents. b) Selectivity is influenced by the nature of substituents. Electron donating substituents deactivate the ring to which they are attached and, consequently, the neighbouring ring is preferably reduced. The more relevant example is the case of compound **11**. Electron-withdrawing substituents activate the ring. Then, although the effect of substitution predominates and reduction of the less substituted ring is mainly produced, an appreciable extent of reduction of the more substituted ring is observed. See for instance compounds **10** and **14**. c) These effects are not in general, and comparing the results obtained with compounds **6–8** it can be observed that the best results are obtained with compound **6**, which has an electron donor substituent, while the presence of a carboxymethyl group in **8** clearly deactivates the reaction. Probably, it is necessary to consider in **6** the effect of the coordination of the oxygen atom with the nanoparticle that will approach the arene to the NP surface, while the interaction with the carbonyl oxygen of the ester group in **8** will put the aromatic ring away from the NP. d) The case of the ketone derivatives is particular since both arene and carbonyl groups are reduced. Thus, when a ketone is present in the substrate like in **12**, **13** and **14**, there is competition between the reduction of the naphthalenic system and that of the ketone. If the ketone is situated in position 1 like in **14**, its reduction is favoured probably because the ketone coordinates preferably with the metal surface rather than the naphthalenic system. If the system becomes more hindered like in **13**, the ketone is hydrogenated preferably.

Overall, this study shows evidence of the good catalytic properties of ruthenium nanoparticles towards arene reduction even for stable compounds such as substituted PAHs.

Experimental

Reagents and general procedures

All syntheses were performed using standard Schlenk techniques under N_2 or Ar atmosphere. Chemicals were purchased from Aldrich Chemical Co, Fluka and Strem. All solvents were distilled over drying reagents and were deoxygenated before use. The precursor [Ru(COD)(COT)] was purchased from Nanomeps. The synthesis of the nanoparticles were performed using 1 L Fischer–Porter and pressurized on a high pressure line.

General procedure for the synthesis of Ru-NPs

In a typical procedure, the [Ru(COD)(COT)] (400 mg, 1268 mmol) was placed into a Fischer–Porter reactor in 400 mL of dry and deoxygenated THF by freeze–pump–thaw cycles in the presence of 0.4 equiv. of PPh_3. The Fischer–Porter reactor was then pressurised under 3 bar of H_2 and stirred for 24 h at room temperature. The initial yellow solution became black after 20 minutes. After elimination of excess dihydrogen, a small amount (approx. 5 drops) of the solution was deposited under an argon atmosphere on a carbon-covered copper grid for transmission electron microscopy analysis (TEM). The rest of the solution was concentrated under reduced pressure to 40 ml. Precipitation and washing with pentane (3 × 15 ml) were then carried out, obtaining a black precipitate.

General procedure for the hydrogenation reactions

In a typical experiment, a 5-entry autoclave or an autoclave Par 477 equipped with PID control temperature and a reservoir for kinetic measurements were charged in a glove-box with 3 mg of Ru nanoparticles (the catalyst concentration was calculated based on the total number of metallic atoms in the NPs) and the substrate in 10 mL of solvent. Molecular hydrogen was then introduced until the desired pressure was reached. The reaction was stirred during the corresponding time at the desired temperature. The autoclave was then depressurised. The solution was filtered over silica and analysed by gas chromatography. The conversion and the selectivities towards the product were determined using a Fisons instrument (GC 9000 series) equipped with a HP-5MS column.

Conversion and selectivity were determined by GC-MS and *cis*/*trans* selectivity was confirmed by NOE experiments in NMR. GC-MS spectroscopy was carried out using a HP 6890A spectrometer, with an HP-5 column (0.25 mm × 30 m × 0.25 μm). The method used for the polyaromatic systems consisted of an initial isotherm period at 130 °C for 10 min followed by a

10 °C min^{-1} temperature ramp to 180 °C with a hold time of 35 min and a flow rate of 3.5 ml min^{-1}.

The method used for the substituted naphthalenes consisted of an initial isotherm period at 40 °C for 3 min followed by a 3 °C min^{-1} temperature ramp to 120 °C with a hold time of 12 min and a flow rate of 1.3 ml min^{-1}.

The retention times for the main products detected for each substrate are detailed below:

- Substrate **1**: tr1 = 2.03 min, tr1a = 1.83 min, tr1b = 1.58 min, tr1c = 1.41 min.

- Substrate **2**: tr2 = 14.91 min, tr2a = 14.22 min, tr2b = 13.15 min, tr2c = 10.73 min, tr2d = 12.76 min, tr2e = 8.37 min.

- Substrate **3**: tr3 = 14.72 min, tr3a = 13.04 min, tr3b = 14.31 min, tr3c = 13.71 min.

- Substrate **4**: tr4 = 46.46 min, tr4a = 44.62 min, tr4b = 41.16 min, tr4c = 36.74 min, tr4d = 20.58 min, tr4e = 21.90 min.

- Substrate **5**: tr5 = 22.80 min, tr5a = 20.80 min, tr5b = 18.27 min.

- Substrate **6**: tr6 = 5.56 min, tr6a = 4.91 min, tr6b = 3.68 min, tr6c = 3.02 min.

- Substrate **7**: tr7 = 27.39 min, tr7a = 25.96 min, tr7b = 23.70 min, tr7c = 20.51 min.

- Substrate **9**: tr9 = 5.46 min, tr9a = 4.55 min, tr9b = 3.39 min, tr9c = 2.90 min.

- Substrate **10**: tr10 = 2.11 min, tr10a = 2.04 min, tr10b = 1.96 min, tr10c = 1.86 min.

- Substrate **11**: tr11 = 7.94 min, tr11a = 6.41 min.

- Substrate **12**: tr12a = 11.56 min, tr12b = 10.79 min, tr12c = 9.21 min.

- Substrate **13**: tr13 = 14.06 min, tr13a = 12.55 min, tr13b = 13.61 min.

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