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Ligand effect in the Rh-NP catalysed partial hydrogenation of substituted arenes†

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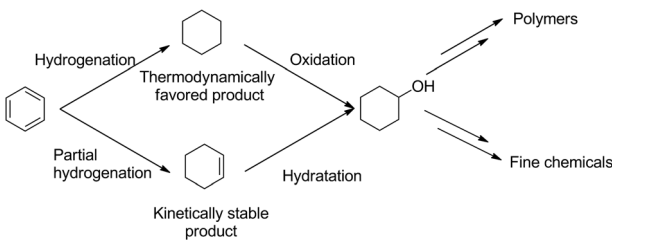
The Rh nanoparticles **Rh1–Rh4** stabilised by the mono- and bidentate phosphine and phosphite ligands **I–IV** were synthesised, characterised and applied as catalysts in the partial hydrogenation of substituted arenes. In the case of disubstituted arenes, selectivities for the corresponding cyclohexene derivatives of up to 39% were achieved at *ca.* 40% conversion. The effect of parameters such as temperature and pressure was also examined. In the hydrogenation of styrene, very high selectivities for ethylbenzene were achieved with TOF values up to *ca.* 23 500 h^{-1}. All these results show that the catalytic performance of small Rh-NPs can be modulated by the appropriate choice of stabilising agents.

Introduction

Over the last decades, transition metal-nanoparticles (M-NPs) have received a great deal of attention as catalysts since they potentially combine the advantages of heterogeneous and homogeneous catalysts, exhibiting high activities while retaining tunability and selectivity through their well defined composition with a narrow size distribution.[1–3] In particular, Ru-NPs have been extensively studied and relevant advances in both their characterisation and catalytic applications have been reported.[4] The stabilisation of M-NPs can be realised in the presence of polymers, surfactants or ligands, which allows the control of their size, shape and dispersion as well as their surface state. The choice of an appropriate stabiliser for the M-NPs is thus of critical importance in tailoring their catalytic performance. For instance, polymer stabilised Rh and Ru-nanoparticles were shown to be highly active in the hydrogenation of arenes, and produce exclusively cyclohexanes.[5] Interestingly, Dyson and co-workers recently showed that the addition of phosphines to Rh-NPs of *ca.* 3 nm in diameter previously synthesised in the presence of PVP improves the selectivity of the NP hydrogenation reactions.[6] They postulated that the selective coordination of these ligands could modify the steric hindrance at specific sites of the NPs and hence generate selectivity. Van Leeuwen, Chaudret and co-workers also recently reported the use of carbene and large bite angle diphosphine ligands as stabilisers for Ru-NPs and their application in the hydrogenation of aromatics, with interesting ligand effects observed.[7]

In the hydrogenation of arenes, the formation of partially hydrogenated products, namely cyclohexenes, is of high interest for the straightforward formation of cyclohexanol *via* hydration (Scheme 1). In this field, several strategies to improve the chemoselectivity for cyclohexenes *vs.* cyclohexanes have been developed and usually involve the competitive displacement of the cyclohexene product from the metal surface prior to its complete hydrogenation.[8–11] For this purpose, modification of heterogeneous catalysts by organic and/or inorganic additives was shown to be efficient. To date, the employment of M-NPs in the partial hydrogenation of arenes has been limited to the use of aqueous reaction media[12] or stabilisers like ionic liquids (ILs)[13–15] where the solubility of the substrate is higher than that of the cyclohexene product. However, high selectivities for cyclohexenes are usually only achieved at low conversions. Masdeu-Bultó and co-workers reported the use of Rh and Ru-NPs stabilised by PPh_3 and its fluorinated derivative $P[3,5\text{-}(CF_3)_2C_6H_3]_3$ in the partial hydrogenation of methylanisoles



Scheme 1 Industrial application of the products formed during the hydrogenation of arenes.

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to cyclohexene derivatives with a selectivity of up to 15% at 21% conversion (yield up to *ca.* 3%) in a sCO_2 reaction medium.[16]

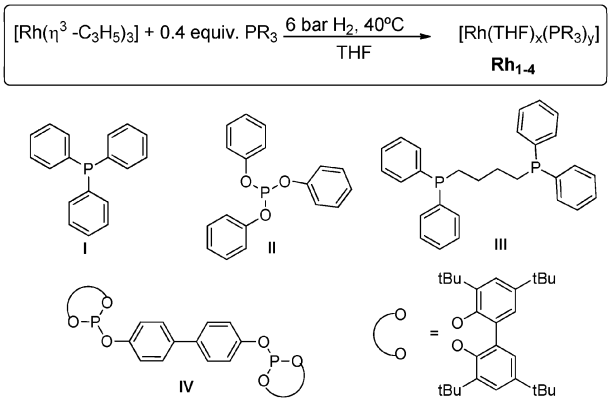
In recent years, our research group has been interested in the use of phosphorus donor ligands as NP stabilisers in selective catalysis. We reported the hydrogenation of arenes using Rh and Ru-NPs stabilised by diphosphites bearing a carbohydrate backbone.[17] These catalytic systems are active in the hydrogenation of methylanisoles in pentane; however, no conversion was obtained when coordinating solvents such as THF and acetonitrile were used.

Here, we report the synthesis and characterisation of a series of P-donor stabilised Rh-NPs and their application in the partial hydrogenation of xylenes and methylanisoles with high selectivity for cyclohexene derivatives, even at relatively high conversion, and in the absence of additives. The objective of this work is the study of the effect of these stabilisers (mono- and bidentate phosphines and phosphites), which is analysed *via* comparison with the catalytic results obtained using NPs stabilised by a mixture of THF and MeOH. The selectivity of these NPs towards the hydrogenation of vinylic *vs.* aromatic double bonds was also investigated using styrene as the substrate.

Results and discussion

Soluble Rh-NPs stabilised by the phosphorus donors **I–IV** (P : Rh = 0.4) (Scheme 2) were synthesised by decomposition of $[Rh(\eta^3\text{-}C_3H_5)_3]$ in THF at 40 °C under 6 bar of H_2. The Rh-NPs were isolated as black powders after precipitation with pentane. These Rh-NPs were characterised by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and elemental analysis.

TEM micrographs of **Rh1–Rh4** revealed in all cases the formation of small Rh-NPs of similar size (*ca.* 1.6 nm diameter, Fig. 1). The **Rh4** NPs were observed to present some degree of agglomeration, which could be due to the ability of the ligand **IV** to act as a bridge between nanoparticles. The mean diameter and size distribution of **Rh1** stabilised by PPh_3 are in agreement with those reported by Masdeu-Bultó and co-workers.[16] Diffuse peaks in the XRD pattern were observed as expected for a homogeneous distribution of very small particles with a face-centred



Scheme 2 P-donor ligands used in this study to stabilise the Rh-NPs **Rh1–Rh4**.

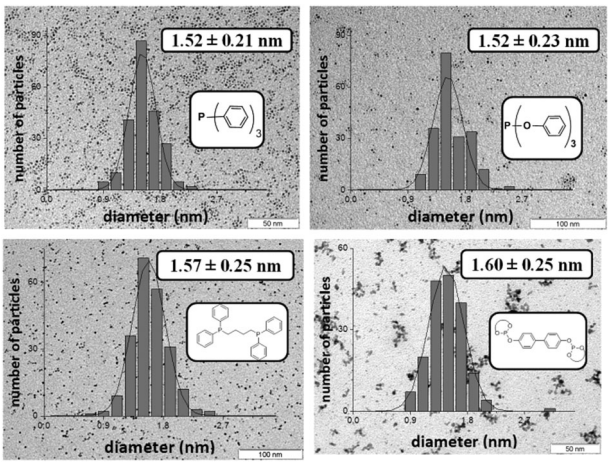


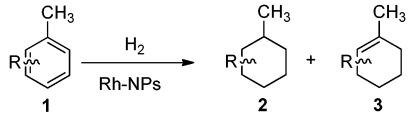
Fig. 1 TEM micrographs and the corresponding size histograms of nanoparticles **Rh1–Rh4**.

cubic (fcc) lattice structure. No reflections arising from rhodium oxides were observed, and coherence lengths with respect to TEM analysis were obtained. XPS measurements were performed on freshly prepared catalyst samples and revealed distinct ratios of $Rh^{\delta+}/Rh^0$ at the surface of **Rh1**, **Rh2** and **Rh4**, while in **Rh3** all of the surface atoms were found to be in the zero-valent state. The theoretical peaks for Rh 3d 5/2 and 3d 3/2 are 307.2 eV and 311.9 eV respectively. These peaks were observed slightly displaced, which may be due to a strong interaction between the Rh nanoparticles and the phosphorus atoms of the stabilising agents. These results are in agreement with XPS data reported for soluble Rh NPs.[18] Elemental analysis of these NPs confirmed the presence of the P-ligands in the NP samples.

Next, the nanoparticles **Rh1–Rh4** were tested in the hydrogenation of methylanisoles **1a–c** at 80 °C for 16 h (Table 1, entries 1–12). In all cases, the *cis* isomers of the corresponding cyclohexane derivatives were the major products. In most cases, under these conditions, the **Rh1** system bearing the triphenylphosphine **I** was found to be the most active catalyst with the highest TON (entries 1, 5 and 9), while the **Rh2** system, stabilised by the triphenylphosphite ligand **II**, was totally inactive (entries 2, 6 and 10). The latter catalyst was also inactive when xylenes were tested as substrates, which indicated that the ligand **II** efficiently blocks the NP surface sites which are responsible for the hydrogenation of the aromatic ring. This result can be explained by the high ligand coverage observed for the **Rh2** NPs (see elemental analysis in ESI†), when compared to the **Rh1** NPs bearing the ligand **I**. When the systems bearing bidentate stabilisers **Rh3** and **Rh4** were used, lower conversions were observed relative to those obtained with **Rh1**. However, **Rh4** produced the partially hydrogenated products with high selectivity (*ca.* 40%) at *ca.* 40% conversion, which corresponds to *ca.* 15% yield. Interestingly, no partially hydrogenated products were detected when the system bearing the diphosphine ligand **III** was used as catalyst.

These results clearly demonstrate that the properties of the P-donor stabilising agents strongly affect the activity and

Table 1 Rh-NP (**Rh1–Rh4**) catalysed hydrogenation of *o*-, *m*-, *p*-xylene (**1a–c**) and *o*-, *m*-, *p*-methylanisole (**1d–f**)[a]



R= OCH_3: *ortho*- (**1a**), *meta*- (**1b**) and *para*-methylanisole (**1c**).

R= CH_3: *ortho*- (**1d**), *meta*- (**1e**) and *para*-xylene (**1f**).

	Subst.	NPs	%Conv.[b]	*cis–trans*[b]	%Sel.3/[%yield][b]	TON[c]
1	**1a**	**Rh1**	>99	98/2	—	147
2	**1a**	**Rh2**	—	—	—	—
3	**1a**	**Rh3**	40	>99	—	53
4	**1a**	**Rh4**	35	>99	36 [13]	124
5	**1b**	**Rh1**	>99	58/42	—	147
6	**1b**	**Rh2**	—	—	—	—
7	**1b**	**Rh3**	19	63/37	—	25
8	**1b**	**Rh4**	38	68/32	39 [15]	135
9	**1c**	**Rh1**	>99	66/34	—	147
10	**1c**	**Rh2**	—	—	—	—
11	**1c**	**Rh3**	32	71/29	—	42
12	**1c**	**Rh4**	49	71/29	21 [10]	174
13	**1d**	**Rh4**	>99	75/25	8 [8]	351
14	**1e**	**Rh4**	51	75/25	15 [8]	181
15	**1f**	**Rh4**	36	67/33	22 [8]	128

[a] General conditions: 1.24 mmol of substrate, 3.5 mg of Rh-NPs, 10 mL of heptane, T = 80 °C, P = 40 bar H_2, t = 16 h. [b] Determined by GC. [c] TON was defined as the number of mol of substrate (**1a–f**) converted per mol of surface Rh. The substrate/Rh ratio was calculated based on elemental analysis data of each NP.

selectivity of Rh-NP catalysts in the hydrogenation of methylanisoles. The selectivity for the partially hydrogenated products in the hydrogenation of methylanisoles observed for the **Rh4** system was found to follow the trend *ortho* ≈ *meta* > *para*, which was attributed to the greater steric hindrance induced by the substituents in *ortho* and *meta* positions.

To investigate the effect of the presence of a coordinating oxygen atom in the substrates **1a–1c**, the corresponding xylene substrates **1d–1f** were examined using **Rh4** as catalyst (Table 1, entries 13–15). Although similar selectivity to cyclohexene derivatives was observed for both *para*-substituted substrates **1c** and **1f** (Table 1, entry 12 *vs.* 15), higher yields of partially hydrogenated products were obtained in the case of *ortho*- and *meta*-methylanisoles compared to their xylene analogues (Table 1, entry 4 *vs.* 13 and entry 8 *vs.* 14). Higher conversions were obtained with xylenes as substrates, which could explain these differences in selectivity. However, when benzene was used as a substrate using **Rh4** as catalyst, cyclohexane was the only reaction product. No significant changes in the size of the NPs were observed by TEM microscopy after catalysis.

To further probe the effect of the stabilising agent, new Rh-NPs were synthesised in the absence of P-donor stabilisers. These NPs were formed following the procedure reported by Chaudret and co-workers to obtain analogous ruthenium nanoparticles.[19] The proportion of solvent (THF–MeOH) was chosen to obtain nanoparticles with similar size to those stabilised with the P-donors **I–IV**. The same rhodium precursor $Rh(\eta^3\text{-}C_3H_5)_3$ was decomposed in the presence of THF and a small amount of MeOH (ratio 97.5 : 2.5), under 4 bar of H_2 at ambient temperature. TEM analysis revealed the presence of small nanoparticles of *ca.* 1.2 nm diameter, slightly smaller than **Rh1–Rh4**. Surprisingly, when the nanoparticles **Rh5** were used in the hydrogenation of *p*-xylene, no catalytic activity was detected. These results indicated that either the substitution of P-donor stabilisers at the surface of these NPs by THF–MeOH or their smaller size was inhibiting the hydrogenation reaction.

To distinguish between these two possibilities, larger NPs were synthesised using the seeded growth method.[20] The TEM micrographs of these NPs revealed the formation of nanoparticles of 1.9 and 2.5 nm diameter. Again, no catalytic activity was observed when these new systems were applied in the hydrogenation of *p*-xylene under the same conditions. It was therefore concluded that the activity and selectivity of **Rh1–Rh4** are mainly governed by the presence of the P-donor stabilising agents **I–IV** and that substitution of these by the mixture of THF and MeOH molecules has an inhibiting effect on their hydrogenation performance.

Next, the effects of temperature and H_2 pressure were studied using the **Rh4** system in the hydrogenation of *p*-xylene during 16 h in heptane. The results are shown in Fig. 2. Under 40 bar of H_2 pressure, when the temperature was increased from 60 °C to 120 °C, a decrease in conversion from 51% to 15% was observed. Conversely, the selectivity towards the partially hydrogenated product increased from 6% to 32%.

These results indicated that the desorption of both the substrate and the cyclohexene derivative product from the NP surface is facilitated by increased temperature, thus lowering the conversion and increasing the selectivity towards the

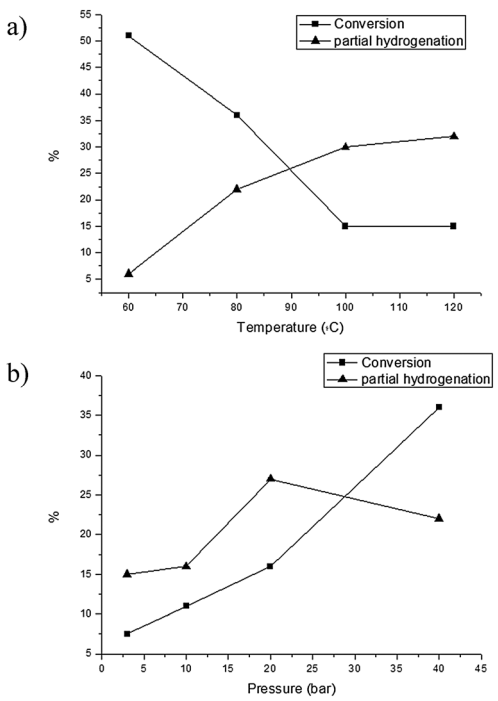


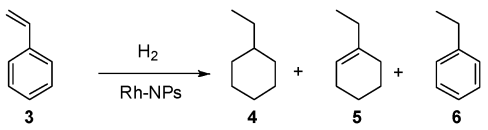
Fig. 2 Effect of pressure and temperature on the partial hydrogenation of *p*-xylene using **Rh4** as catalyst (general conditions: 1.24 mmol of substrate, 3.5 mg of Rh-NPs, 10 mL of heptane, t = 16 h; [a] P = 40 bar of H_2; [b] T = 80 °C).

partially hydrogenated product, as previously reported for heterogeneous catalysts.[21] At 80 °C, when the pressure was increased from 3 to 40 bar of H_2, conversion increased from 7% to 36%. Interestingly, the selectivity for the partially hydrogenated product was also improved and reached a maximum of 27% at 20 bar of H_2, but decreased again when 40 bar of H_2 pressure was used. It is accepted that hydrogenation of aromatics occurs in a consecutive manner and hydrogen pressure affects the different steps of aromatic ring hydrogenation in different ways. Odenbrand and Lundin reported that the hydrogenation of cyclohexenes to cyclohexanes is less dependent on H_2 pressure than the hydrogenation of aromatics to cyclohexenes.[22] With an increase in hydrogen pressure, the rate of hydrogenation of the aromatic ring to cyclohexene apparently increases faster than the rate of hydrogenation of cyclohexene to cyclohexane, resulting in the higher selectivity for cyclohexene formation. However, when the pressure is further increased, both rates are higher, which results in a higher yield of total hydrogenation.

To compare the selectivity of our catalysts in the hydrogenation of vinylic and aromatic C=C double bonds, the Rh NPs **Rh1–Rh5** were tested in the hydrogenation of styrene. The results are shown in Tables 2 and 3.

When the catalytic reactions were performed at 80 °C (Table 2), full conversions were obtained with all the systems after 1 h. In most cases, the selectivity for the totally hydrogenated product **4** increased once the vinylic group was reduced. Interestingly, under these conditions, the aromatic ring of styrene was hydrogenated even using the **Rh5** system, which was totally inactive in the hydrogenation of *p*-xylene at 80 °C (entries 9 and 10). This result suggests that increased steric hindrance in the case of the xylene substrate was inhibiting the reaction. In contrast, total selectivity for ethylbenzene **6** was achieved using **Rh2** as catalyst (entries 3 and 4), even after 16 h of reaction time, suggesting that the monophosphite ligand **II** efficiently blocks the coordination sites of the Rh-NPs required for the hydrogenation of the aromatic ring of styrene. Under these conditions, yields of up to 18% of partially hydrogenated products were detected when **Rh1** or **Rh4** was employed. It is noteworthy that these values were obtained at complete conversion of the substrate. The higher activities obtained with styrene compared to those obtained with disubstituted substrates (Table 1) can be explained by the lower steric hindrance associated with the presence of only one substituent on the aromatic ring.

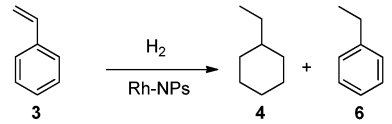
Table 2 Rh-NP (**Rh1–Rh5**) catalysed hydrogenation of styrene at 80 °C[a]



	t (h)	NPs	%Conv.[b]	%4[b]	%5[b]	%6[b]	TON[c]
1	1	**Rh1**	100	27	0	73	124
2	16	**Rh1**	100	65	18	17	124
3	1	**Rh2**	100	2	0	98	320
4	16	**Rh2**	100	3	0	97	320
5	1	**Rh3**	100	29	0	71	110
6	16	**Rh3**	100	100	0	0	110
7	1	**Rh4**	100	67	9	24	295
8	16	**Rh4**	100	76	16	8	295
9	1	**Rh5**	100	14	8	78	86
10	16	**Rh5**	100	91	3	5	86

[a] General conditions: 3.5 mg of Rh-NPs, 1.24 mmol of styrene, 10 mL of heptane, T = 80 °C, P = 40 bar H_2. [b] Determined by GC. [c] TON was defined as the number of mol of substrate (**3**) converted per mol of surface Rh.

Table 3 Rh-NP (**Rh1–Rh4**) catalysed hydrogenation of styrene at RT[a]



	t (h)	NPs	%Conv.[b]	%4[b]	%6[b]	TON[c]	TOF[c] (h^{-1})
1	0.25	**Rh1**	27	0	100	1460	5842
2	1	**Rh1**	100	8	92	5409	—
3	16	**Rh1**	100	15	85	5409	—
4	0.25	**Rh2**	5	0	100	699	2795
5	1	**Rh2**	24	0	100	3354	3354
6	16	**Rh2**	84	0	100	11 738	—
7	0.25	**Rh3**	23	0	100	1103	4414
8	1	**Rh3**	54	0	100	2591	2591
9	16	**Rh3**	100	2	98	4797	—
10	0.25	**Rh4**	46	0	100	5924	23 696
11	1	**Rh4**	100	0	100	12 878	—
12	16	**Rh4**	100	11	89	12 878	—
13	0.25	**Rh5**	65	0	100	2426	9705
14	1	**Rh5**	100	0	100	3733	—
15	16	**Rh5**	100	21	79	3733	—

[a] General conditions: 3.5 mg of Rh-NPs, 54 mmol of styrene (5 mL), 5 mL of heptane, T = RT, P = 40 bar H_2. [b] Determined by GC. [c] TON was defined as the number of moles of substrate (**3**) converted per mol of surface Rh. TOF was calculated at styrene conversions lower than 65% and it is defined as the mol of substrate (**3**) converted per mol of surface Rh per hour. The substrate/Rh ratio was calculated based on elemental analysis data of each NP.

To obtain selectivity data at lower conversions, the reaction was performed at ambient temperature using a much larger ratio of substrate to Rh (54 mmol of styrene, 1 : 1 volume ratio with heptane) (Table 3). In all cases, ethylbenzene **6** was the major reaction product. No partially hydrogenated products were detected when the reaction was performed at this temperature, in agreement with the results presented in Fig. 2a. After 15 minutes of reaction time, conversions between 5 and 65% were obtained with total selectivity for ethylbenzene **6**, corresponding to TOFs up to *ca.* 23 500 h^{-1} using **Rh4** (Table 3, entry 10). **Rh2**, stabilised by $P(OPh)_3$ **II**, was once again the least active catalyst: after 16 h at this temperature, the totally hydrogenated product **4** was detected in all cases except for this catalyst (Table 3, entry 6). These results clearly show that the nature of the stabilising ligand affects the catalytic performance of these highly active nanocatalysts.

Conclusions

In summary, the hydrogenation of substituted arenes such as styrene, xylenes and methylanisoles was investigated using

soluble Rh-NPs as catalysts, and results showed relevant differences in activity and selectivity depending on the properties of the NP-stabilising P-ligand used. For instance, large differences in activity and selectivity were observed for **Rh1** and **Rh2**, stabilised by triphenylphosphine **I** and triphenylphosphite **II**, respectively. The presence of the P-ligand was shown to be critical: the THF–MeOH-stabilised **Rh5** was inactive in the hydrogenation of xylenes, although hydrogenation of both the aromatic ring and the vinylic group of styrene was observed. In the case of disubstituted arene substrates, selectivities for the corresponding cyclohexene derivatives of up to 39% were achieved at *ca.* 40% conversion. The effect of parameters such as temperature and pressure was also examined. In the hydrogenation of styrene, very high selectivities for ethylbenzene were achieved with TOF values up to *ca.* 23 500 h^{-1}. All these results show that the catalytic performance of small Rh-NPs can be modulated by the appropriate choice of stabilising agents.

Experimental section

General procedure for the synthesis of the Rh-NPs

In a typical procedure, the $[Rh(\eta^3\text{-}C_3H_5)_3]$ (64 mg, 0.28 mmol) was placed into a Fischer–Porter reactor at −110 °C (acetone/N_2 bath) in 64 mL of dry and deoxygenated (by freeze–pump–thaw cycles) THF in the presence of the appropriate ligand (0.2 equiv. for bidentate ligands and 0.4 equiv. for monodentate ligands). The Fischer–Porter reactor was then pressurised under 6 bar of H_2 and stirred for 30 minutes at room temperature. The solution was then heated to 40 °C and stirred at this temperature for 24 h. The initial colourless solution became black after 1 h. A small amount (approx. 20 drops) of the solution was deposited under an argon atmosphere on a carbon-covered copper grid for transmission electron microscopy (TEM) analysis. The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 × 15 mL) was then carried out, to obtain a black precipitate.

Synthesis of rhodium nanoparticles stabilised by a mixture of solvents

In a typical procedure, the $[Rh(\eta^3\text{-}C_3H_5)_3]$ (64 mg, 0.28 mmol) was placed into a Fischer–Porter reactor, and a mixture of solvents THF–MeOH in a 97.5 : 2.5 volume ratio was added. The Fischer–Porter reactor was then pressurised under 4 bar of H_2 and stirred at room temperature for 16 h. The solution became black immediately. A small amount (approx. 5 drops) of the solution was deposited under an argon atmosphere on a carbon-covered copper grid for TEM analysis. The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 × 15 mL) was then carried out, to obtain a black precipitate.

General procedure for the synthesis of the Rh-NPs using the seeded-growth method

In a typical procedure, the corresponding mixture of solvents (THF–MeOH 97.5 : 2.5) of 32 mL containing $[Rh(\eta^3\text{-}C_3H_5)_3]$ (32 mg, 0.14 mmol) was added to a half THF–MeOH solution of previously prepared Rh-NPs (0.14 mmol of Rh). The reaction mixture was placed in a Fischer–Porter reactor, which was then pressurised under 4 bar of H_2 and stirred at room temperature for 16 h. A small amount (approx. 5 drops) of the solution was deposited under an argon atmosphere on a carbon-covered copper grid for TEM analysis. The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 × 15 mL) was then carried out, to obtain a black precipitate.

General procedure for the hydrogenation reactions

In a typical experiment, a 5 entries autoclave was charged in the glove-box with Rh nanoparticles (3.5 mg) and the substrate (1.24 mmol, approx. substrate to Rh ratio = 100) in 10 mL of heptane. Molecular hydrogen was then introduced until the desired pressure was reached. The reaction was stirred for 16 h at the appropriate temperature. The autoclave was then depressurised. The solution was filtered over Celite and analysed by gas chromatography. The conversion and the *cis*-selectivity of the product were determined using a Fisons instrument (GC 9000 series) equipped with a HP-5MS column.

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