



# Hydrogenation of arenes, alkenes and alkynes catalyzed by a sol–gel entrapped mixture of $[\text{Rh}(\text{cod})\text{Cl}]_2$ and $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$

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## ABSTRACT

A sol–gel entrapped 1:3 mixture of  $[\text{Rh}(\text{cod})\text{Cl}]_2$  and  $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$  catalyzes the hydrogenation of various unsaturated substrates by two distinguishable mechanisms. Under 13.8 bar  $\text{H}_2$  and 20 °C methylated arenes react rapidly to give cycloalkane derivatives. XRD and TEM studies showed that under these conditions the hydrogenation proceeds without the generation of free metal particles. The hydrogenation of non-methylated arenes, as well as that of alkenes and alkynes, require a temperature of 80–120 °C at which the entrapped complexes form metallic nano-particles of 3–5 nm. Chloroarenes are also hydrodechlorinated at 120 °C, but require a hydrogen pressure of  $\geq 25$  bar. At both temperature ranges the catalysts are reusable at least four times. The high efficiency of the hydrogenation process at 20 °C is rationalized by a synergistic effect between the two different metal atoms of the combined catalyst. This may be related to a remote control model through a hydrogen spillover mechanism.

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## 1. Introduction

Synergism between different metal nuclei in heteropolymetallic complexes that causes an increase in the reaction rates and/or significant changes in the regio-, chemo- and stereo-selectivity in catalysts has been well defined [1,2] and documented [3]. Synergism has been observed not only in complexes but also in alloys in which the two metals are in close proximity. In these systems the synergism is attributed mainly to a combination of electronic and geometric effects [4,5]. A similar mutual effect between different metals has also been identified in reactions by catalysts composed of a silica-supported metal complex and a silica-tethered different free metal. Notable are the pioneering studies in this field by Angelici and his associates who used mainly palladium as the “free metal” and various complexes of rhodium as the “soluble part” of the combined catalyst [6–14]. Here the synergism has been explained by a hydrogen spillover process [6–15]. However, in a similar combined system in which both the palladium particles and the rhodium complex are entrapped within a silica sol–gel matrix, the involvement of a spillover process in arene hydrogenation and in arene hydrodefunctionalization has been shown to be unlikely

[16–20]. Furthermore, Bianchini and his associates proved in a very elegant comprehensive study that in the hydrogenation of benzene by silica supported palladium together with the sulfur containing silica tethered [(1,2,5,6- $\eta$ )-1,5-cyclooctadiene][4-[3-(diphenylphosphino- $\kappa$ P)-2,2-bis(diphenylphosphino- $\kappa$ P)methylpropyl]benzenesulfonatorhodium, both metals activate the substrate, and the palladium and rhodium atoms are linked to each other by a metal–metal bond throughout the catalytic cycle [21,22]. In this paper we report on a recyclable hydrogenation catalyst composed of two multi-homonuclear complexes  $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$  and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (without added free metal) between which synergism is observed when entrapped within a rigid silica sol–gel matrix. This combined catalyst was found to operate by completely different mechanisms at 20 °C and above 80 °C.

## 2. Experimental

### 2.1. Instruments

Infrared spectra were run on a Bruker model Vector 22 FTIR machine.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AMX-300 and AMX-400 instruments. Mass spectra were measured on a Hewlett-Packard model 4989A mass spectrometer equipped with a HP gas chromatograph model 5890 spectrometer. 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

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column packed with Carbowax 20 M-poly(ethylene glycol) in fused silica (Supelco 25301-U). X-ray powder diffraction measurements were performed on the D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a goniometer radius 217.5 mm. Göbel Mirror parallel-beam optics, 2° Sollers slits and 0.2 mm receiving slit. Low-background quartz sample holders were carefully filled with the powder samples. The specimen weight was 0.2 g approximately. XRD patterns within the range 8–78° 2 $\theta$  were recorded at room temperature using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) with following measurement conditions: tube voltage of 40 kV, tube current of 40 mA, step-scan mode with a step size of 0.02° 2 $\theta$  and counting time of 1 s/step. Transmission electron microscopy was done with scanning transmission electron microscope (STEM) Tecnai G<sup>2</sup> F20 (FEI Company, USA) operated at 200 kV and equipped with EDAX EDS for identification of elemental composition. Initial powders were dispersed in ethanol and dropped onto a standard 400 mesh carbon coated copper TEM grid. Inductively Coupled Plasma (ICP) analyses were performed with the aid of a PerkinElmer model Optima 3000 instrument. Surface areas and average pore diameters of the sol-gel matrices were measured using a Micrometrics ASAP 2020 instrument.

## 2.2. Chemicals

Di- $\mu$ -chlorobis[(1,2,5,6,- $\eta$ )-1,5-cyclooctadiene]dirhodium [23], sodium 1,2- $\mu$ -carbonyl-1,1,1,2,2,2,3,3,3,3-decacarbonyl-1,2- $\mu$ -hydro-triangular-triruthenate(1-) [24], *cis,cis*-1,3,5-trimethylcyclohexane [25], *cis,trans*-1,3,5-trimethylcyclohexane [26] and 5-chloro-1,2,3,4-tetrahydronaphthalene [27] were synthesized and identified according to published procedures. All other chemicals were obtained from commercial sources.

## 2.3. Preparation of sol-gel entrapped catalysts

A mixture of 1.7 ml tetramethoxysilane TMOS and 1.3 ml of triply distilled water was stirred under N<sub>2</sub> at 40 °C for 3 min. A solution of 42.6 mg (6.67  $\times 10^{-2}$  mmol) of Na[HRu<sub>3</sub>(CO)<sub>11</sub>] and 11.3 mg (2.23  $\times 10^{-2}$  mmol) of [Rh(cod)Cl]<sub>2</sub> in 3 ml of degassed THF was added. Gelation started within 10 min. The gel was left for aging during 24 h and dried at 1 torr and 100 °C for another 24 h to give 0.7 g of the immobilized combined catalyst. The average N<sub>2</sub>-BET surface area of the resulting sol-gel material was 662  $\pm$  6 m<sup>2</sup>/g with pore diameter of 33–34 Å. Likewise, 8.89  $\times 10^{-2}$  mmol of [Rh(cod)Cl]<sub>2</sub> and 8.89  $\times 10^{-2}$  mmol of Na[HRu<sub>3</sub>(CO)<sub>11</sub>] were entrapped separately in silica sol-gel matrices for comparative studies.

## 2.4. General procedure for the hydrogenation experiments

Typically, a Parr bench teflon-lined mini autoclave equipped with a sampling device and a stirrer was placed in a thermostat regulated to the desired temperature and charged with 6.67 mmol of the substrate, the above described entrapped catalyst (containing 0.089 mmol metals), and if applicable, 3–5 ml of a solvent. The reaction vessel was flushed three times with N<sub>2</sub>. The nitrogen was replaced by H<sub>2</sub> and the autoclave pressurized to 13.8 bar and the mixture was stirred for the required length of time. After cooling to 0 °C the liquid phase was decanted and the ceramic catalyst washed with 30 ml of CH<sub>2</sub>Cl<sub>2</sub>. The combined liquid phases were analyzed for leached rhodium and ruthenium species by ICP, concentrated and the products compared with authentic samples. The liquid phases were tested also for residual catalytic activity. In none of these experiments could any catalytic activity of the liquid phases be detected. The recovered sol-gel material was sonicated for 20 min

with 30 ml of CH<sub>2</sub>Cl<sub>2</sub>, dried for 4 h at 1 torr and 100 °C before reapplication in a second catalytic run.

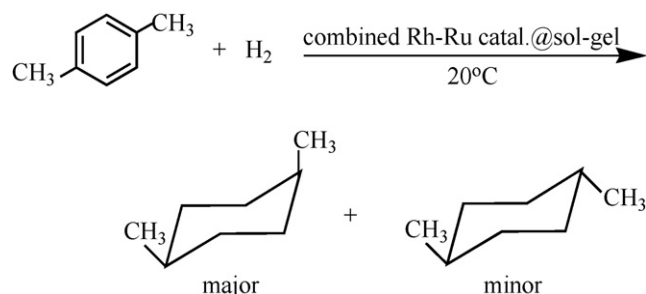
## 2.5. Hydrogen transfer experiments

Typically, a mini-autoclave was placed in an airless glove box, charged with 0.7 g of silica sol-gel material in which 42 mg (0.066 mmol) of Na[HRu<sub>3</sub>(CO)<sub>11</sub>] had been entrapped. The autoclave was flushed three times with pure (99.999%) N<sub>2</sub>. The nitrogen was then replaced by H<sub>2</sub> and pressurized to 13.8 bar. After 19 h at 20 °C, the autoclave was opened within the glove box and flushed with N<sub>2</sub>. To the reaction vessel was added a mixture of 11.3 mg (0.023 mmol) of [Rh(cod)Cl]<sub>2</sub>, 0.707 g (6.67 mmol) of *p*-xylene and 5 ml of *n*-heptane. The autoclave was sealed and the mixture was stirred magnetically at 20 °C (now under 2.3 bar N<sub>2</sub>). After 21 h the vessel was opened under an ambient atmosphere, the immobilized catalyst was filtered off and the filtrate worked-up as described above. GC, NMR and mass spectral analyses revealed the presence of 33% of *cis*- and 11% of *trans*-1,4-dimethylcyclohexane admixed with 56% of unreacted *p*-xylene. When the first part of the reaction was conducted just under 1 bar of H<sub>2</sub>, the yields of the *cis*- and *trans*-dimethylcyclohexane were 9 and 5%, respectively.

Experiments in which the first step of the process, was the treatment of the sol-gel entrapped [Rh(cod)Cl]<sub>2</sub> (0.023 mmol) for 19 h with H<sub>2</sub> (13.8 bar) at 20 °C and the second step was the addition of 0.067 mmol of Na[HRu<sub>3</sub>(CO)<sub>11</sub>] in 1.5 ml MeOH under N<sub>2</sub> together with 6.67 mmol of *p*-xylene to the hydrotreated encaged rhodium complex, resulted after 21, in the complete recovery of the unreacted *p*-xylene.

## 3. Results and discussion

Hydrogenation of *p*-xylene at 20 °C under 13.8 bar H<sub>2</sub> for 2 h in the presence of a heterogenized catalyst, prepared from a 1:3 molar mixture of [Rh(cod)Cl]<sub>2</sub> and Na[HRu<sub>3</sub>(CO)<sub>11</sub>] and hydrolyzed tetramethoxysilane (TMOS) gave a quantitative yield of 1,4-dimethylcyclohexanes (Scheme 1). The ratio between the *cis*- and *trans*-isomers of the product was usually 3.5:1. If the used ceramic catalyst was filtered off, washed and sonicated with CH<sub>2</sub>Cl<sub>2</sub>, it could be reused in a second run of the same or of another hydrogenation process. The filtrate, however, proved to be absolutely inactive and metal-free. In a typical series of hydrogenations of *p*-xylene conducted with the same (recycled) catalyst under the above conditions for 1 h the yields in the first four runs were 87% (63-*cis*, 24-*trans*), 67% (49-*cis*, 18-*trans*), 69% (51-*cis*, 18-*trans*) and 72% (54-*cis*, 18-*trans*), respectively. The decrease in yield after the first run is not uncommon in reactions with sol-gel entrapped catalysts. In leach-proof processes, as in ours, this change in activity has usually been rationalized by partial clogging of the pores by substrate and/or product molecules (see, e.g., Refs. [16–20]). However, in the present study the dimensions of the pores hardly



Scheme 1. Hydrogenation of *p*-xylene.

changed when the catalyst was recycled. For example, the average pore diameters of the immobilized combined catalyst before and after the hydrogenation of *p*-xylene were found by N<sub>2</sub>-BET measurements to be 3.84 and 3.80 Å, respectively, and the corresponding pore volumes were 0.618 and 0.602 cm<sup>3</sup>/g. Thus, the reason for the yield decrease after the first run (though not in the more advanced ones) in our case seems not to be associated with pore clogging.

The yield of the hydrogenation of *p*-xylene at 20 °C proved to depend strongly on the molar ratio between the entrapped rhodium and ruthenium complexes (see Table 1). Both metallic complexes are, however, essential for an efficient hydrogenation process. While the immobilized combined catalysts containing [Rh(cod)Cl]<sub>2</sub> and Na[HRu<sub>3</sub>(CO)<sub>11</sub>] ([Rh]:[Ru] = 1:3) promoted quantitative hydrogenation of the arene within 2 h at 20 °C, the entrapped ruthenium complex alone gave under the same conditions only 48% of 1,4-dimethylcyclohexanes (36 and 12% of the respective *cis*- and *trans*-isomers) and the immobilized rhodium complex was found to have hardly any catalytic power. The silica sol-gel support was also shown to be essential. A stirred mixture (500 rpm, 20 °C) of the non-entrapped rhodium and ruthenium complexes (in 1:3 ratio) in *p*-xylene was found to be almost inactive and the slow formation of metallic particles was observed. By raising the temperature from 20 to 80 °C the mixture of Rh and Ru complexes decomposes rapidly in the presence of hydrogen to give an inactive metal mirror.

Apart from *p*-xylene, the combined entrapped catalyst promotes also fast hydrogenation of other methylated benzene at 20 °C (see Table 2). Non-substituted arenes (see entries 1 and 5) require however, a temperature of at least 80 °C and aromatics with electron withdrawing groups (entries 6, 8 and 9) react only at, or above, 100 °C and need a considerably longer reaction period. The hydrogenation of nitrobenzene (entry 7) takes place only at 120 °C and affords just aniline rather than aminocyclohexane. Initially we tried to rationalize this unexpected observation that electron donating substituents lead to the enhancement of the hydrogenation of aromatic C–C bonds either by the ability of electron-rich arenes to facilitate the π-bonding of the substrate to the metal atoms [28–30], or by the activation of the catalyst by the benzylic hydrogen atoms in methylated arenes as in the case of [(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>NCH<sub>3</sub>]<sup>+</sup>[RhCl<sub>4</sub>]<sup>−</sup> catalyzed hydrogenations [31]. However, as we found that the addition of toluene to the reaction mixture of benzene (or naphthalene) did not enhance the formation of the alicyclic products, we ruled out these explanations. Hydrodechlorination of chloroarenes is, under the conditions of Table 2 at 13.8 bar, rather sluggish but proceeds smoothly when the hydrogen pressure is increased to 27.6 bar.

Alkenes also require an elevated temperature for efficient hydrogenation. For example, 1-octene, which undergoes initially extensive double bond migration, forms after 1 h at 20 °C a mixture of just 11% of octane, 45% of internal octenes and 44% of unreacted starting material. Only after raising the temperature to 80 °C complete transformation of the mixture to octane could be accomplished.

The hydrogenation of alkynes requires even more harsh conditions than that of alkenes and takes place usually in a stepwise fashion. Phenylacetylene forms at 120 °C initially styrene which is further hydrogenated to ethylbenzene only after most of the alkyne has been consumed (cf. Ref. [31]). Further hydrogenation thereafter is however difficult as polymerization of the styrene becomes significant after 3–4 h.

The influence of the bulkiness of the substrate on the rate of hydrogenation is notable. While *p*-xylene is converted at 20 °C under the conditions of Table 2 into 87% of isomeric 1,4-dimethylcyclohexanes within 1 h, the sterically hindered *o*-xylene

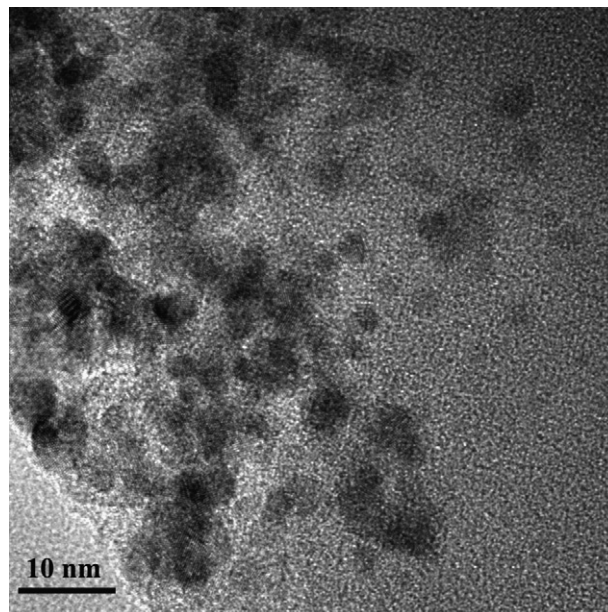


Fig. 1. Transmission electron micrograph of metal particles formed during the hydrogenation of *p*-xylene in the presence of silica sol-gel entrapped [Rh(cod)Cl]<sub>2</sub> and Na[HRu<sub>3</sub>(CO)<sub>11</sub>] at 120 °C and 13.8 bar H<sub>2</sub> for 4 h. The dark areas represent the free metallic particles.

yields during this period only 20% of the respective cycloalkanes.

Further investigation of the hydrogenation reactions of *p*-xylene and the other substrates listed in Table 2, showed that those performed at 20 °C follow in fact a different pathway than those carried out above 80 °C. The latter ones are usually substantially slower than the low temperature reactions and do not require a 1:3 molar ratio of the rhodium to the ruthenium complex. Even *p*-xylene reacts slower at 80 °C than at 20 °C and forms after 2 h under the conditions of Table 2 only 17% of the isomeric 1,4-dimethylcyclohexanes. Likewise, the hydrogenation products of mesitylene dropped from 100% after 3 h at 20 °C to 39% after 4 h at 80 °C. XRD and TEM studies clearly indicated that while at 20 °C the entrapped combined catalyst does not form any metal particles, at, or above, 80 °C, nano-particles of 3–5 nm composed of 63–75% Ru and 25–37% of Rh are obtained (Fig. 1). It should be noted that the free metal particles are neither formed during the preparation of the immobilized catalyst nor in the drying process at 100 °C. Their formation requires the presence of dihydrogen. As the reaction mixtures at 80–120 °C, from which the sol-gel material has been removed by filtration, do not contain any free Ru or Rh particles, it can be concluded that the metal particles formed are securely entrapped within the ceramic matrix. Since in various hydrogenations of aromatic C–C bonds [32,33], as well as in some other catalyses [34], the catalytic activity is attributed to the involvement of metallic nano-particles, we assume that also in our experiments above 80 °C the metallic species take part in the catalytic process.

In experiments that were carried out above 80 °C we did not observe synergism between the metallic particles, and in some cases as for example in the hydrodechlorination of 1-chloronaphthalene we found even that the entrapped nano-particles generated from [Rh(cod)Cl]<sub>2</sub> are more efficient than either those formed from Na[HRu<sub>3</sub>(CO)<sub>11</sub>] or from the mixture of both complexes.

In light of the observation that at 20 °C the hydrogenation of methylated benzenes proceeds by the combined catalyst without formation of metallic nanoparticles, we assume that the reduc-

**Table 1**Dependence of the hydrogenation of *p*-xylene on the molar ratio of [Rh(cod)Cl]<sub>2</sub> and Na[HRu<sub>3</sub>(CO)<sub>11</sub>] within the ceramic catalyst<sup>a</sup>

Ratio of {[Rh(cod)Cl] <sub>2</sub> }:{Na[HRu <sub>3</sub> (CO) <sub>11</sub> ]}	Total yield (%) <sup>b</sup>	Yield of <i>cis</i> -isomer (%) <sup>b</sup>	Yield of <i>trans</i> -isomer (%) <sup>b</sup>
1:1	14	11	3
1:2	25	16	9
1:3	87	63	24
1:4	41	25	16
1:5	25	19	6

<sup>a</sup> Reaction conditions: 6.67 mmol of *p*-xylene, 0.7 g of sol-gel matrix containing a total of 0.089 mmol of Ru and Rh complexes; 13.8 bar H<sub>2</sub>; 20 °C; 1 h.<sup>b</sup> In the first run.

tion of these substrated may be associated at least in part, with a remote control model such as that developed by Delmon and his co-workers [35–37]. In this model the synergism is related to a hydrogen spillover species, which migrates, from one of the complexes to the other one. Such a mechanism was shown to take place particularly in the presence of metals and metal oxides, but it was observed also when metallic molecular compounds were used as catalysts [38]. Support for the involvement of spillover hydrogen in the hydrogenation of *p*-xylene at 20 °C was found in a series of experiments in which the substrate was reacted in a two-stage process. First the entrapped ruthenium-containing component of the catalyst had been treated alone with H<sub>2</sub> (13.8 bar) at 20 °C. The reaction vessel was then opened in an air-less, glove box and the sol-gel material flushed with pure nitrogen. To the immobilized hydrogen-treated ruthenium compound was added the non-entrapped rhodium complex dissolved in a mixture of *p*-xylene and *n*-heptane. The molar ratio of the entrapped Na[HRu<sub>3</sub>(CO)<sub>11</sub>], the free [Rh(cod)Cl]<sub>2</sub> and the xylene was 3:1:300. Stirring of the combined components under 2.3 bar N<sub>2</sub> afforded after 21 h the two hydrogenation products of the xylene, *cis*- and *trans*-1,4-dimethylcyclohexane in 33 and 11%, respectively, despite the fact that the entrapped complexes were present only in catalytic quantities. If we assume that the N<sub>2</sub>-BET value of 662 m<sup>2</sup>/g is approximately the surface area available for absorption of the hydrogen on the entrapped ruthenium catalyst, this gas is roughly the amount required for the formation of the aforementioned amount of dimethylcyclohexanes. When the hydrogen pressure in the first stage of the process was reduced to 1 bar, the hydrogenation still took place but the yield of the cyclohexane formed during 21 h decreased to 14%. Experiments in which the [Rh(cod)Cl]<sub>2</sub> has been treated with H<sub>2</sub> in the first stage followed by the addition of the Na[HRu<sub>3</sub>(CO)<sub>11</sub>] in *p*-xylene and MeOH failed

to form any hydrogenation products. This may indicate that the hydrogen transfer takes place from the ruthenium to the rhodium component.

Further support for our assumption that the hydrogenation of methylated arenes involves hydrogen spillover was found in some IR and <sup>1</sup>H NMR studies. We have shown that the mixing of Na[HRu<sub>3</sub>(CO)<sub>11</sub>] and [Rh(cod)Cl]<sub>2</sub> at 20 °C is not associated with a chemical reaction. In the mixture of the complexes all the characteristic absorption bands of the ruthenium complex (KBr pellets) appear at 2085, 2051, 2044, 2029, 2000, 1978 and 1602 cm<sup>-1</sup> and those of the rhodium compound at 1324, 995, 960 and 815 cm<sup>-1</sup> (cf. Refs. [39,40]), and the <sup>1</sup>H NMR contains the resonance peaks of the rhodium complex at 1.75, 2.50 and 2.23 ppm. However, when the mixture of complexes was subjected to H<sub>2</sub> at 20 °C, the characteristic IR and <sup>1</sup>H NMR peaks of the rhodium complex disappear completely within ca. 20 min owing to the deposition of the free metal. When the mixture of the complexes was entrapped within the silica sol-gel the absorption peaks broadened but the presence of [Rh(cod)Cl]<sub>2</sub> could still be detected after 4 h. Soxhlet extraction of the ceramic matrix gave a mixture of compounds whose <sup>1</sup>H NMR spectra showed clearly the presence of the *dimeric* rhodium complex free of non-coordinated 1,5-cyclooctadiene. All these experiments seem to support the existence of a spillover mechanism though with the data at hand we cannot exclude completely the formation of some Rh–Ru species that may be responsible for the observed synergism in the hydrogenation of the methylated arenes.

Finally, it is notable that although the hydrogenations listed in Table 2 follow two different mechanisms, in both the active immobilized catalysts can be recovered and recycled at least four times with hardly any loss of catalytic activity after the second run.

**Table 2**Hydrogenation experiments by sol-gel-entrapped [Rh(cod)Cl]<sub>2</sub> and Na[HRu<sub>3</sub>(CO)<sub>11</sub>]<sup>a</sup>

Entry	Substrate	Temperature (°C)	Time (h)	Solvent	Products (yield in the first run, %) <sup>b</sup>
1	Benzene	80	2	None	Cyclohexane (31)
2	Toluene	20	1	None	Methylcyclohexane (75)
3	<i>o</i> -Xylene	20	1	None	<i>cis</i> -1,2-Dimethylcyclohexane (20)
4	Mesitylene	20	3	None	<i>cis,cis</i> -1,3,5-Trimethylcyclohexene (86); <i>trans,cis</i> -1,3,5-trimethylcyclohexene (14)
5	Naphthalene	80	20	DCE <sup>c,d</sup>	<i>cis</i> -Decaline (87), <i>trans</i> -decaline (12)
6	Ethyl benzoate	100	8	<i>n</i> -Heptane	Ethyl cyclohexanecarboxylate (63)
7	Nitrobenzene	100	24	<i>n</i> -Heptane	Aniline (78)
8	2-Chlorophenol <sup>e</sup>	120	24	<i>n</i> -Dodecane	Cyclohexanone (53); cyclohexane (44)
9	1-Chloronaphthalene <sup>e</sup>	120	24	<i>n</i> -Heptane	5-Chloro-1,2,3,4-tetrahydronaphthalene (39); tetralin (23); <i>cis</i> -decalin (19); <i>trans</i> -decalin (<1)
10	1-Octene	80	2	None	Octane (99)
11	Phenylacetylene	120	2	DCE <sup>c</sup>	Styrene (42); ethylbenzene (43)

<sup>a</sup> Reaction conditions: 0.7–0.8 g sol-gel containing 6.67 × 10<sup>-2</sup> mmol Ru complex and 2.23 × 10<sup>-2</sup> Rh complex; 6.67 mmol substrate; 5 ml solvent (if applicable); 13.8 bar H<sub>2</sub> (except for entries 8 and 9).<sup>b</sup> The yields are average of at least two experiments that did not differ by more than ±3%. The missing percentages reflect on the unreacted starting compound.<sup>c</sup> 1,2-Dichloroethane.<sup>d</sup> 3 ml.<sup>e</sup> 27.6 bar H<sub>2</sub>.

#### 4. Conclusions

The co-entrapment of  $[\text{Rh}(\text{cod})\text{Cl}]_2$  and  $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$  within a silica sol-gel matrix forms a recyclable hydrogenation catalyst that operates via two distinguishable pathways. A 1:3 molar ratio of the rhodium to ruthenium complex promotes rapid hydrogenation of methylated benzene molecules to give the corresponding cyclohexane derivatives already at 20 °C. At that temperature the hydrogenation seems to proceed, at least partially, by a remote control pathway. This conclusion is based on the experiments in which the rhodium-free immobilized  $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$  was found to adsorb hydrogen that is transferable to a non-entrapped solution of  $[\text{Rh}(\text{cod})\text{Cl}]_2$  in *p*-xylene and on IR and NMR studies of the immobilized metal compounds which indicate the presence of unchanged starting complexes after their mixing and after treatment with hydrogen. The spillover hydrogen may then be responsible for the hydrogenation of the aromatic substrate. When the hydrogenation was carried out at  $\geq 80$  °C the combined entrapped catalyst formed metallic nano-particles that promote not only the hydrogenation of the methylated arenes but also that of nitro- and chloro-arenes as well as of alkenes and alkynes. These reactions proceed however, at a lower rate than the hydrogenations at 20 °C (in which no metallic particles have been found by XRD and TEM studies). Whereas the reaction at 20 °C are associated with synergism between the rhodium and ruthenium atoms of the combined catalyst, no such effect has been observed in the high temperature processes.

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