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Hydrogenation of arenes, alkenes and alkynes catalyzed by a sol–gel entrapped mixture of $[Rh(cod)Cl]_2$ and $Na[HRu_3(CO)_{11}]$

Raed Abu-Reziq[a,*], Margarita Shenglof[b], Liza Penn[b], Tomer Cohen[b], Jochanan Blum[b,**]

[a] Sol-Gel Technologies, Industrial Zone West, Bet Shemesh 99100, Israel
[b] Department of Organic Chemistry, The Hebrew University, Givat Ram, Jerusalem 91904, Israel

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ABSTRACT

A sol–gel entrapped 1:3 mixture of $[Rh(cod)Cl]_2$ and $Na[HRu_3(CO)_{11}]$ catalyzes the hydrogenation of various unsaturated substrates by two distinguishable mechanisms. Under 13.8 bar 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.

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-η)-1,5-cyclooctadiene][4-[3-(diphenylphosphino-κP)-2,2-bis(diphenylphosphino-κP)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 $Na[HRu_3(CO)_{11}]$ and $[Rh(cod)Cl]_2$ (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

Infared spectra were run on a Bruker model Vector 22 FTIR machine. ^1H and ^{13}C NMR spectra were recored 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 chromatic 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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[*] Corresponding author. Tel.: +972 2 9997661; fax: +972 2 9999066.
[**] Corresponding author. Tel.: +972 2 6585329; fax: +972 2 6513832.
E-mail addresses: raed.abu-reziq@sol-gel.com (R. Abu-Reziq), jblum@chem.ch.huji.ac.il (J. Blum).

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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 speciment weight was 0.2 g approximately. XRD patterns within the range 8–78° 2θ were recorded at room temperature using Cu Kα radiation ($\lambda = 1.5418$ Å) with following measurement conditions: tube voltage of 40 kV, tube current of 40 mA, step-scan mode with a step size of 0.02° 2θ and counting time of 1 s/step. Transmission electron microscopy was done with scanning transmission electron microscope (STEM) Tecnai G^2 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-μ-chlorobis[(1,2,5,6,-η)-1,5-cyclooctadiene]dirhodium [23], sodium 1,2-μ-carbonyl-1,1,1,2,2,2,3,3,3,3-decacarbonyl-1,2-μ-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_2 at 40 °C for 3 min. A solution of 42.6 mg (6.67×10^{-2} mmol) of $Na[HRu_3(CO)_{11}]$ and 11.3 mg (2.23×10^{-2} mmol) of $[Rh(cod)Cl]_2$ 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_2-BET surface area of the resulting sol–gel material was $662 \pm 6\,m^2/g$ with pore diameter of 33–34 Å. Likewise, 8.89×10^{-2} mmol of $[Rh(cod)Cl]_2$ and 8.89×10^{-2} mmol of $Na[HRu_3(CO)_{11}]$ 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_2. The nitrogen was replaced by H_2 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_2Cl_2. 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_2Cl_2, dried for 4 h at 1 torr and 100 °C before reapplication in a second catalytic run.

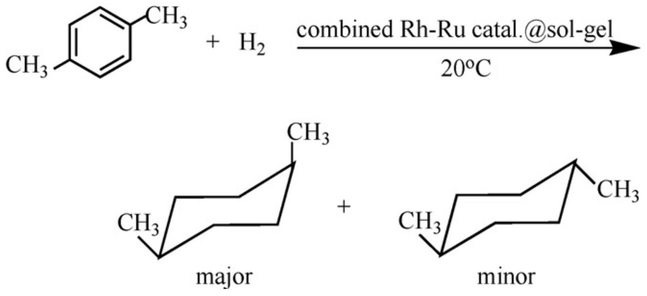
2.5. Hydrogen transfer experiments

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 $Na[HRu_3(CO)_{11}]$ had been entrapped. The autoclave was flushed three times with pure (99.999%) N_2. The nitrogen was then replaced by H_2 and pressurized to 13.8 bar. After 19 h at 20 °C, the autoclave was opened within the glove box and flushed with N_2. To the reaction vessel was added a mixture of 11.3 mg (0.023 mmol) of $[Rh(cod)Cl]_2$, 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_2). 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_2, 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 $[Rh(cod)Cl]_2$ (0.023 mmol) for 19 h with H_2 (13.8 bar) at 20 °C and the second step was the addition of 0.067 mmol of $Na[HRu_3(CO)_{11}]$ in 1.5 ml MeOH under N_2 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_2 for 2 h in the presence of a heterogenized catalyst, prepared from a 1:3 molar mixture of $[Rh(cod)Cl]_2$ and $Na[HRu_3(CO)_{11}]$ 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_2Cl_2, 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.