SUPPORTING INFORMATION

Ligand effect in the Rh-NPs catalysed partial hydrogenation of substituted arenes.

Jessica Llop Castelbou, Aitor Gual, Elisabet Mercadé, Carmen Claver* and Cyril Godard*

Table of contents:

S1. General, materials and characterization techniques.

S2. Synthesis of the diphosphite 4 derived from 4-4'-dihydroxydiphenyl

S3. Synthesis of Rhodium [Rh(η^3-(C5H5))3] precursor from RhCl3·3H2O

S4. Synthesis of rhodium nanoparticles stabilized by P-ligands

S5. Synthesis of rhodium nanoparticles stabilized by mixture of solvents


S7. Characterization of the rhodium nanoparticles Rh1-Rh5

S8. Catalytic experiments

S9. References
S1. General, materials and characterization techniques.

**General methods.** All syntheses were performed using standard Schlenk techniques under N\textsubscript{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 Rh(η\textsubscript{3}-C\textsubscript{3}H\textsubscript{5})\textsubscript{3}, was prepared following previously described methods\cite{1,2}. The synthesis of Rh-nanoparticles were performed using 200ml Fisher Porter and pressurized on a high pressure line.

The deuterated solvents for NMR measurements were dried over molecular sieves. \textsuperscript{1}H, \textsuperscript{13}C {\textsuperscript{1}H}, and \textsuperscript{31}P {\textsuperscript{1}H} NMR spectra were obtained on a Varian Mercury 400 MHz spectrometer. Chemical shifts were calibrate relative to SiMe\textsubscript{4} (\textsuperscript{1}H and \textsuperscript{13}C NMR) as internal standard or 85\% H\textsubscript{3}PO\textsubscript{4} as external standard (\textsuperscript{31}P NMR).

The TEM experiments were performed at the “Unitat de Microscopia dels Serveis Cientificotècnics de la Universitat Rovira I Virgili” (TEM-SCAN) in Tarragona with a Zeiss 10 CA electron microscope operating at 100 kV with resolution of 3 Å. The particles size distributions were determined by a manual analysis of enlarged images. At least 300 particles on a given grid were measured in order to obtain a statistical size distribution and a mean diameter.

XRD measurements were made using a Siemens D5000 diffractometer (Bragg- Brentano parafocusing geometry and vertical 0-0 goniometer) fitted with a curved graphite diffracted- beam monochromator, incident and diffracted- beam Soller slits, a 0.06° receiving slit and scintillation counter as a detector. The angular 2θ diffraction range was between 26 and 95°. The data were collected with an angular step of 0.05° at 16s per step and sample rotation. A low background Si(510) wafer was used as sample holder. Cu\textsubscript{Kα} radiation was obtained from a copper X-ray tube operated at 40kV and 30mA.

GS-MS spectroscopy was carried out on a HP 6890A spectrometer, with an achiral HP-5 column (0.25mm x 30m x 0.25um), T°C= 250°C injector, flow 1.5ml/min.

XPS experiments were performed in a PHI 5500 Multitechnique System (from Physical Electronics) with a monochromatic X-ray source (Aluminium Kalfa line of 1486.6 eV energy and 350 W), placed perpendicular to the analyzer axis and calibrated using the 3d5/2 line of Ag with a full width at half maximum (FWHM) of 0.8 eV. The analyzed area was a circle of 0.8 mm diameter, and the selected resolution for the spectra was 187.5eV of Pass Energy and 0.8 eV/ step for the general spectra and 23.5 eV of Pass Energy and 0.1 eV/step for the spectra of the different elements in the depth profile spectra. A low energy electron gun (<10 eV) was used in order to discharge the surface when necessary. All measurements were performed in a ultra high vacuum (UHV) chamber pressure between 5x10\textsuperscript{-9} and 2x10\textsuperscript{-8} torr.
S2. Synthesis of the diphosphite 4 derived from 4'-4'-dihydroxydiphenyl

4,4',6,6'-Tetra-tert-butyl-2,2'-bisphenol (0.9g, 2.2mmol) was dissolved in 30ml of dry and degassed toluene. Degassed pyridine (2.13ml, 27mmol) was added carefully to 0.46 mL of distilled PCl₃ at 0ºC. The bisphenol solution was slowly added to the PCl₃/pyridine solution. The reaction was stirred during 16h at 60ºC to form the 4,4',6,6'-tetra-tert-butyl-2,2'-biphenylphosphochloridrite. The pyridine salts formed were removed by filtration under argon atmosphere. The reaction mixture was concentrated under reduced pressure and the product was used without purification in the following reaction (estimated yield 90%).

4'-4'-dihydroxydiphenyl (0.149g, 0.8mmol, 1eq) was dissolved in 4mL of dry and degassed toluene. 4,4',6,6'-tetra-tert-butyl-2,2'-biphenylphosphochloridrite (0.94g, 1.97mmol, 2.1eq) was dissolved in 3.12 mL of degassed pyridine (38.7 mmol). The 4'-4'-dihydroxydiphenyl solution was added to the phosphochloridite/pyridine solution and the mixture stirred overnight at room temperature. Purification was carried out by column chromatography under nitrogen with dry and degassed toluene as eluent, yielding 4 as a white solid (yield 400mg, 85%).

1H NMR (400MHz, toluene d₈, δ in ppm): δ =7.62 (d, J=2.4Hz, 4H), 7.38 (d, J=2.4Hz, 4H), 7.13 (d, J= 8Hz, 4H), 7.08 (d, J= 8Hz, 4H), 1.61 (s, 36H, 'Bu-ortho), 1.28 (s, 36H, 'Bu-para).

13C NMR (400MHz, toluene d₈, δ in ppm): δ =151.9 (d, JPC= 6 Hz, -C), 147.1 (-C- Ar), 146.3 (d, JPC=6Hz, -C-), 140.7 (-C- Ar), 136.45 (-C- Ar), 133.8 (d, JPC= 3Hz, -C-), 128.3 (CH-), 127.15 (CH-), 124.6 (d, JPC= 6Hz, -CH), 122.0 (d, JPC= 8Hz, -CH), 35.7 (-CIV-, 'Bu), 34.7 (-CIV-, 'Bu), 31.5 (CH3-, 'Bu), 31.4 (CH3-, 'Bu).

31P NMR (400MHz, toluene d₈, δ in ppm): δ =145.19

S3. Synthesis of Rhodium [Rh(η⁵-(C₅H₅))₃] precursor from RhCl₃ 3H₂O

The synthesis was carried out according to the procedure described in the literature.[1][2]

Allylmagnesium bromide (35mmol) was added to a cold suspension (-10ºC) of RhCl₃ 3H₂O (1.1g, 5.3 mmol) in THF (93 ml). The solution slowly lost its red-brown color to become yellow. The solution was then allowed to warm to room temperature and stirred for an additional 16 hours. The solvent was removed under reduced pressure and the residue extracted with pentane (previously distilled and deoxygenated) (3x20mL). The sublimation was carried out in a water bath at 40 ºC and the formation of yellow crystals was observed onto the cold finger. (Yield= 520mg, 55%)

S4. Synthesis of rhodium nanoparticles stabilized by P-ligands

The synthesis of the Rh nanoparticles was carried out following the method reported by Chaudret and co-workers.[3] In a typical procedure, the [Rh(η⁵-(C₅H₅))₃] (64 mg, 0.28 mmol) was placed into a Fischer-Porter reactor and dissolved at -110ºC (acetone/ N₂ bath) in 64 mL of dry and deoxygenated THF (using freeze-pump-thaw techniques) in the presence of the appropriate ligand (0.2 equivalents for bidentate ligands and 0.4 equivalents for monodentate ligands). The Fischer-Porter reactor was then pressurized under 6 bar of H₂ and stirred for 30 minutes at
room temperature. The solution was then heated to 40°C and stirred at this temperature during 24 h. The initial colorless solution became black after 1 h. A small amount (5 drops approx.) of the solution was deposited under an argon atmosphere on a carbon-covered copper grid for transmission electron microscopy analysis. The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 x 15 ml) was then carried out, obtaining a black precipitate. (Yield = ca. 25-30 mg, 30-35%)

S5. Synthesis of rhodium nanoparticles stabilized by a THF/MeOH mixture of solvents

The synthesis of the Rh nanoparticles was carried out following the method reported by Chaudret and co-workers.[4] In a typical procedure, the [Rh(η^3-(C_3H_5)₃)] (64 mg, 0.28 mmol) was placed into a Fischer-Porter reactor, a mixture of solvents THF/MeOH in a 97.5:2.5 ratio was added. The Fischer-Porter reactor was then pressurized under 4 bar of H2 and stirred at room temperature during 16 h. The solution became black immediately. A small amount (5 drops approx.) of the solution was deposited under an argon atmosphere onto a carbon-covered copper grid for transmission electron microscopy analysis. The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 x 15 ml) was then carried out, obtaining a black precipitate. (Yield = ca. 10-15 mg, 35-40%)


In a typical procedure, the corresponding mixture of solvents (THF/MeOH 97.5:2.5) of 32 mL containing [Rh(η^3-(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).[5] The reaction mixture was placed in a Fischer-Porter reactor, which was then pressurized under 4 bar of H2 and stirred at room temperature during 16 h. A small amount (5 drops approx.) of the solution was deposited under an argon atmosphere onto a carbon-covered copper grid for transmission electron microscopy analysis (TEM). The rest of the solution was concentrated under reduced pressure. Precipitation and washing with pentane (3 x 15 ml) was then carried out, obtaining a black precipitate.
S7. Characterization of the rhodium nanoparticles Rh1-Rh5

**Rh1**: Nanoparticles stabilized by PPh₃

**TEM:**

Elemental analysis: 4.57 % P, 36.49 % Rh

XRD: hcp crystalline Rh nanoparticles, coherence length $1.49 \pm 0.034$ nm

XPS: 0-30% of Rh⁺⁺ at the surface of the NPs.
Rh2: Nanoparticles stabilized by P(OPh)₃

TEM

Elemental analysis: 4.59% P, 14.12% Rh.

XRD: hcp crystalline Rh nanoparticles, coherence length 1.53 ± 0.023 nm

XPS: 100% of Rh(0) at the surface of the NPs.
**Rh3**: Nanoparticles stabilized by dppb

**TEM:**

Elemental analysis: 4.41% P, 41.83% Rh

XRD: hcp crystalline Rh nanoparticles, coherence length $1.49 \pm 0.07$ nm

XPS: 100% of Rh(0) at the surface of the NPs.
**Rh4**: Nanoparticles stabilized by the diphosphite 4

**TEM:**

[Image of TEM analysis showing nanoparticle size distribution with a peak at 1.60 ± 0.25 nm in diameter (nm) and a scale bar of 50 nm.]

Elemental analysis: 2.09 % P, 15.56 % Rh

**XRD:** hcp crystalline Rh nanoparticles, coherence length 1.43 ± 0.02 nm

[Graph showing XRD pattern with peaks labeled 2θ degrees and sqrt(counts).]

XPS: 0-30% of Rh⁶⁺ at the surface of the NPs.
Rh5: Nanoparticles stabilized by THF/MeOH

TEM:

Elemental analysis: 47.46 % Rh

TEM pictures of THF/MeOH nanoparticles synthesised by seeded growth method
S8. Catalytic experiments

In a typical experiment, a 5 entries autoclave was charged in the glove-box with 3.5 mg of Rh nanoparticles and 1.24 mmol of the substrate in 10 ml of heptane. Molecular hydrogen was then introduced until the desired pressure was reached. At the end of the reaction, the autoclave was depressurized and the solution was filtered over celite and analyzed by Gas Chromatography. The identification of the reaction products were performed by GC-MS and the quantification by GC-FID on a HP 6890A spectrometer with an HP-5 column (0.25mm x 30m x 0.25um), T°= 205°C injector, flow 1.5ml/min.

In the following sections, the GC-MS chromatograms of the hydrogenation reactions are displayed:

(Note: the drawing do not represent the absolute configuration of the products)

Chromatogram of heptane used as solvent
Hydrogenation of o- methylanisole
- Hydrogenation of \textit{m}-methylanisole
- Hydrogenation of \( p\)-methylanisole
- Hydrogenation of \textit{o-} xylene
Electronic Supplementary Material (ESI) for Catalysis Science & Technology
This journal is © The Royal Society of Chemistry 2013
Hydrogenation of \( m \)-xylene
Hydrogenation of $p$-xylene
- Hydrogenation of styrene
Example of a TEM micrograph of the nanoparticles after catalytic experiments.
S9. References