

# A solid iridium catalyst for diastereoselective hydrogenation

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## Chemicals

Pd/C (5 % on activated wood carbon) was a Strem Chemicals product. The HRTEM analysis (Figure 1) of the catalyst shows regular particles with a diameter smaller than 5 nm. A few bigger clusters are nevertheless met (Figure 2). Oxygen chemisorption measurements showed a Pd dispersion of 40%, corresponding to a mean diameter of 2.8-2.9 nm, in accordance with TEM observations.

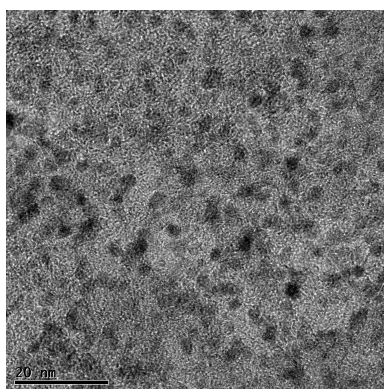


Figure 1: TEM picture of the Pd/C catalyst.

The synthesis of the iridium complex  $[\text{Ir}(\text{cod})(\text{MesImPr})]\text{BF}_4$  and supported complex M-Ir were published in a previous paper [1]. Briefly,  $[\text{Ir}(\text{cod})(\text{MesImPr})]\text{BF}_4$

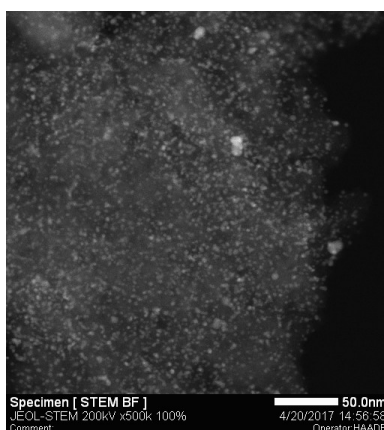


Figure 2: STEM-HAADF micrograph of the Pd/C catalyst.

10 was prepared from a silver carbene and  $[\text{Ir}(\text{cod})\text{Cl}]_2$ . M-Ir was prepared by trans-  
 metallation between  $[\text{Ir}(\text{cod})\text{Cl}]_2$  and the supported silver carbene complex, M-Ag;  
 the latter being obtained by contacting  $\text{Ag}(\text{OCCF}_3)_3$  and a mesostructured silica  
 material containing regularly distributed imidazolium (MesImPr) units at the sur-  
 face of its 2D hexagonal porous network. Such surface imidazolium group were  
 15 generated by contacting the corresponding imidazole with iodopropyl surface frag-  
 ments at the surface of an hybrid silica; the latter<sup>[2]</sup> being synthesized accord-  
 ing to the following protocol: The material was prepared by pre-hydrolysis of  
 TEOS and propyltriethosylsilane in an acidic solution of HI (pH = 1.5) contain-  
 ing a block copolymer namely P123 for 3 hours a RT. The resulting solution was  
 20 further heated up to 45 °C and a catalytic amount of NaF was added to allow a fast  
 co-condensation of the two hydrolyzed precursors. The resulting suspension was  
 further left a 45 °C for two days under stirring before filtration and washings with  
 water, ethanol and ether. The surfactant was further removed by soxhlet extraction  
 and the resulting solid was dried under vacuum at 120 °C.

25 (-)-Terpinen-4-ol (Sigma-Aldrich, 95 % of both enantiomers, enantiomeric ra-  
 tio= 2:1) was dried on 0.5 nm molecular sieves.

Toluene was purified by SPS system and additionally dried with activated 0.5 nm  
 molecular sieves.

### Analysis of the products

30 The reaction was monitored by GC using HP-INNOWAX column (L=30m, d-  
 0.320mm, f=0.25 $\mu\text{m}$ ) and a FID detector. The oven program was the following:  
 50 °C for 2 min, then 10 °C/min to 220 °C for 5 min, then 20 °C/min to 250 °C for  
 2 min. The total run time was 27 min. The retention times were: trans-p-menthan-  
 4-ol at 12.27 min, cis-p-menthan-4-ol at 12.65 min and terpinen-4-ol at 13.37 min  
 35 (checked by injection of pure products, alone or in mixture). An example is pro-  
 vided in Figure 3.

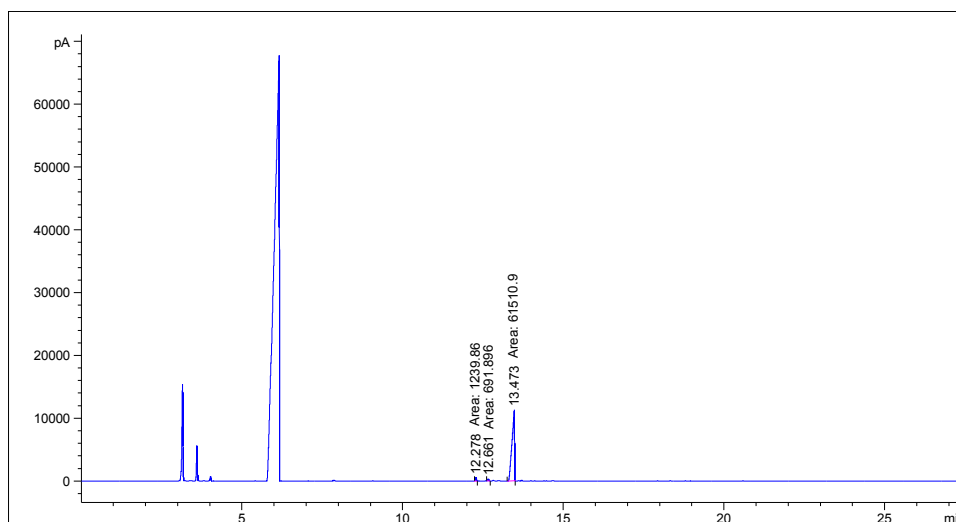


Figure 3: Example of GC analysis.

## Transmission electron microscopy

Transmission Electron Microscopy (HRTEM) of M-Ir and Pd/C solids was performed at the “Centre Technologique des Microstructures”, Université Lyon 1, Villeurbanne, France, with a JEOL2100F transmission electron microscope, using an acceleration voltage of 200 kV. The samples were prepared with copper grids covered with an amorphous carbon film.

## Catalytic tests

Turnover numbers (TONs) are defined as 
$$\text{TON} = \frac{n_{\text{terpinenol}} \times \text{conversion}_{\text{terpinenol}}}{n_{\text{total metal}}}$$

The hydrogenation reactions were carried out in a TOP-industrie stainless steel autoclave of 300 mL (equipped with baffles) stirred at 1500rpm by a gas-inducing turbine. Pd/C (10-100 mg of powder) was first reduced in situ in the solvent during 30 minutes under the reacting conditions (40 or 80 °C, 3 bars); the reactant was then added to the mixture. In the case of M-Ir (50-350 mg of powder), it was introduced in a sealed glass vial together with the reacting solution. After purging the reactor with nitrogen, the vial was broken by the rotating turbine and then, hydrogen was introduced. During the reaction, hydrogen was fed to the semi-batch reactor at constant pressure (3 bar) via a pressure regulator. It was supplied from an upstream calibrated reservoir. The pressure decrease in this reservoir yielded the hydrogen consumption rate and thus the reaction rate. In the case of terpinen-4-ol hydrogenation, the diastereoselectivity of the reaction was measured by GC (see above).

## References

- 60 [1] I. Romanenko, D. Gajan, R. Sayah, D. Crozet, E. Jeanneau, C. Lucas, L. Leroux, L. Veyre, A. Lesage, L. Emsley, E. Lacôte, C. Thieuleux, *Angewandte Chemie International Edition* **2015**, *54*, 12937–12941.
- [2] J. Alauzun, A. Mehdi, C. Reyé, R. Corriu, *New Journal of Chemistry* **2007**, *31*, 911–915.