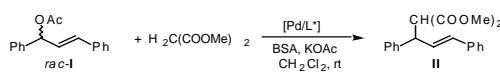
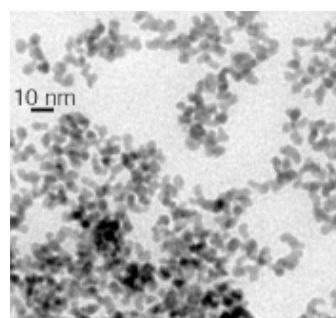
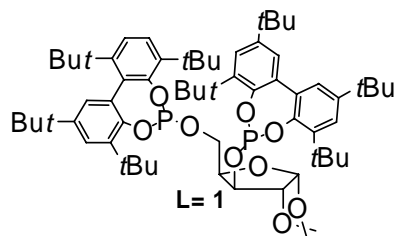
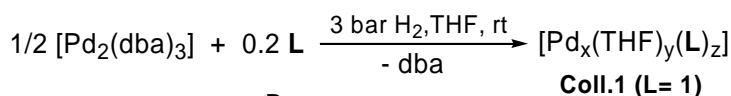


## Metal nanoparticles in catalysis

The organometallic approach followed in the laboratory allows to access to **well-controlled** and **reproducible nanoparticles of various metals** (Pt, Pd, Ru, Rh,...) with higher surface atom numbers when their size decreases. The size control of the particles, and consequently the control of the number of surface active sites in one hand, and the possibility to tune their surface state through ligand addition in another hand, makes these systems very interesting for catalytic applications. At this day, the interest of the use of metal nanoparticles synthesised in the laboratory for catalytic applications has been shown for **olefins** and **aromatic derivatives hydrogenation reactions** as well as for **allylic alkylation reactions**

**Example : chiral diphosphite stabilized Pd nanoparticles used in allylic alkylation : allylic alkylation of *rac*-3-acetoxy-1,3-diphenyl-1-propene (*rac*-I) with dimethyl malonate** has been studied using **chiral diphosphite stabilized Pd nanoparticles** synthesised from the Pd(dba)<sub>2</sub> precursor (d<sub>m</sub>4 nm), and a molecular complex prepared with the same ligand for comparison; similar enantiomeric excesses were observed for the obtained products, but the nanoparticles catalyse the reaction for only one of the enantiomers of the racemic substrate giving rise to a **kinetic resolution on the substrate**, phenomenon non observed with the molecular system. These results show an **original and very interesting behaviour** of the nanoparticles.



Entry	Catalyst	I/Pd/L <sup>a</sup>	Time (h)	Conv. (%) <sup>b</sup>	ee II (%) <sup>c</sup>	ee I (%) <sup>c</sup>
1	Coll.1	100/1/0.2	24	56	97 (S)	89 (S)
2	Coll.1	100/1/0.2	168	59	97 (S)	89 (S)
3	Coll.1	100/1/1.05	168	61	97 (S)	89 (S)

<sup>a</sup> Molar ratio between I, Pd and excess ligand added in the catalysis.<sup>10</sup> <sup>b</sup> Determined by <sup>1</sup>H NMR. <sup>c</sup> Determined by HPLC on a Chiracel-OD column. Absolute configurations of I<sup>13c</sup> and II<sup>15</sup> in parentheses.

The organometallic synthetic method developed in the laboratory can also be applied for the **synthesis of metal nanoparticles onto the surface or inside the pores of inorganic porous materials** (silica, alumina, organised mesoporous materials, alumina membranes,...) leading to **supported catalysts** displaying controlled nanoparticles in size and dispersion. Such nanocatalysts can be synthesized through *in situ* metal precursors decomposition, eventually in a fluidized bed.

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