# SUPRANANO

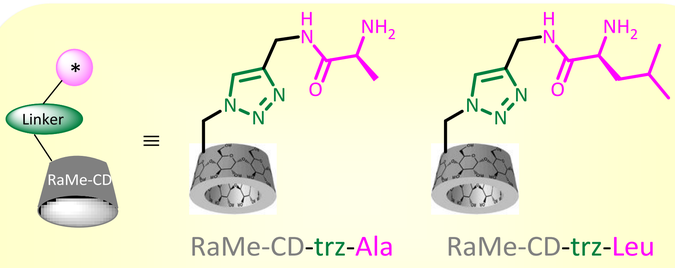
## Ruthenium nanoparticles stabilized by chirally modified cyclodextrins
## Application in supramolecular asymmetric catalysis

Programme Blanc-2009


**N. T. T. Chau,[a] S. Handjani,[a] M. Guerrero,[b] S. Menuel,[c] F. Hapiot,[c] E. Monflier,[c] K. Fajerwerg,[b] K. Philippot,[b] A. Denicourt-Nowicki[a] and A. Roucoux[a]**

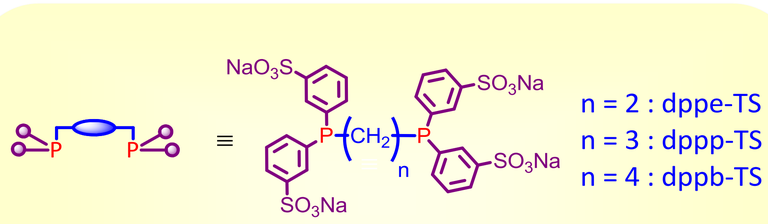
[a] ENS Chimie de Rennes, UMR CNRS 6226, Avenue du Général Leclerc CS 50837, 35708 Rennes cedex 7
[b] Université de Toulouse, UPS, INPT, CNRS, Laboratoire de Chimie de Coordination (LCC), 205 route de Narbonne, F-31077 Toulouse cedex 4
[c] Université d'Artois, UMR CNRS 8181, Unité de Catalyse et de Chimie du Solide (UCCS), Rue Jean Souvraz, SP 18 – F-62307, Lens cedex


## Functionalized cyclodextrins and/or water soluble alkyl sulfonated diphosphines used for stabilization of $Ru^0$ NPs

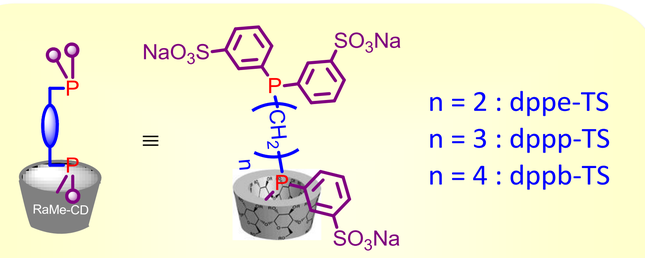



R = H, Me: Randomly methylated β-cyclodextrin (RaMe-CD)

**Chirally modified cyclodextrins**



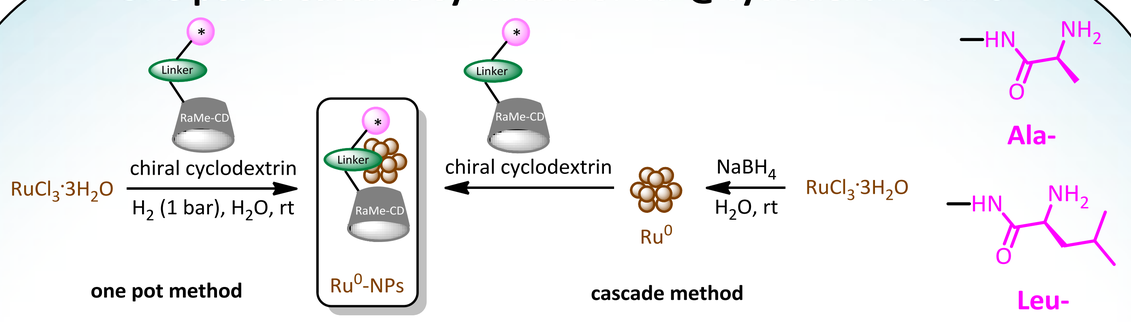

**Alkyl sulfonated diphosphines**

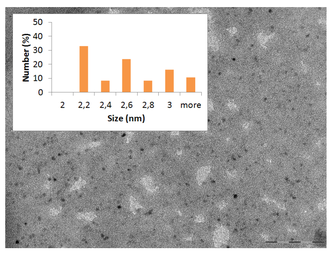



R = H, Me: Randomly methylated β-cyclodextrin (RaMe-CD)

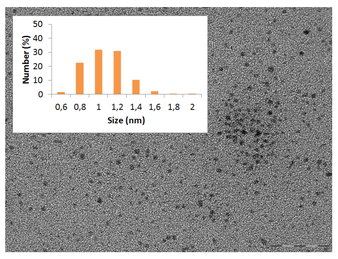
**Cyclodextrin-diphosphine inclusion complex**

## One pot & Cascade synthesis of $Ru^0$@cyclodextrins NPs



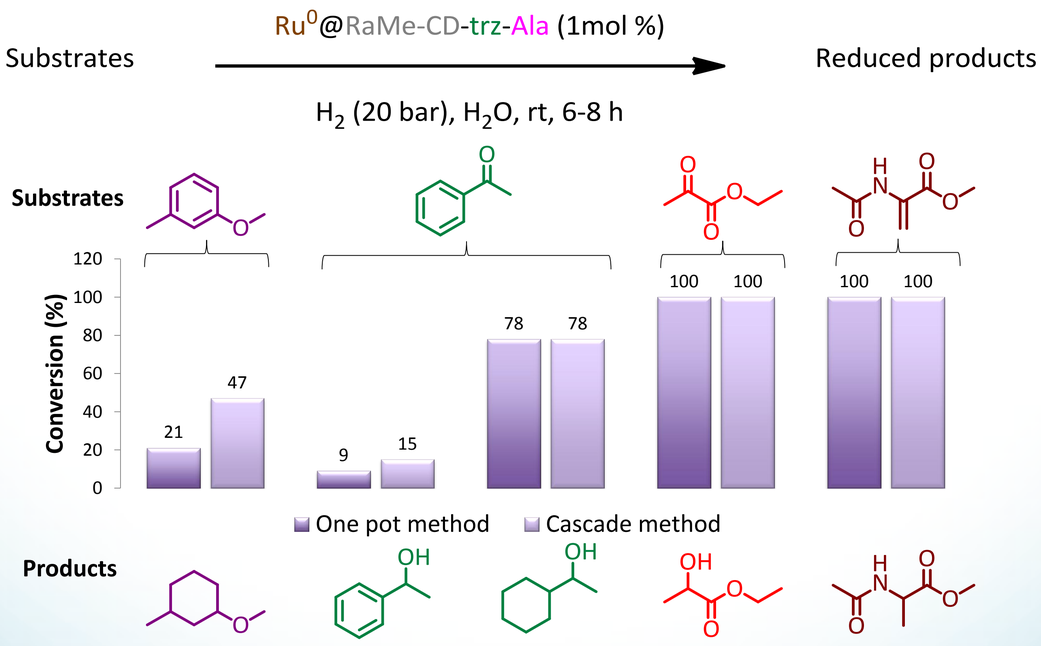




$Ru^0$@RaMe-CD-trz-Ala NPs
by one-pot method (2.5 ± 0.4 nm)



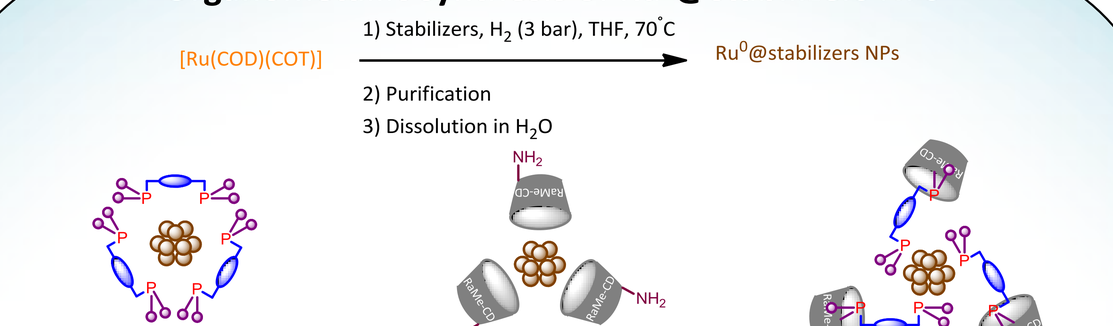

$Ru^0$@RaMe-CD-trz-Ala NPs
by cascade method (1.0 ± 0.2 nm)

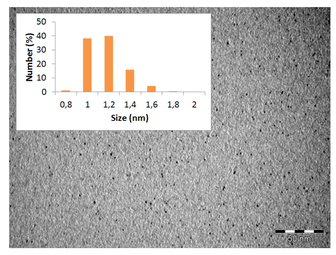
### Reactivity of $Ru^0$@RaMe-CD-trz-Ala NPs



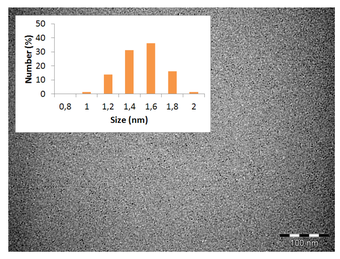

The same catalytic activity was also observed with $Ru^0$@RaMe-CD-trz-Leu NPs

## Organometallic synthesis of $Ru^0$@stabilizers NPs

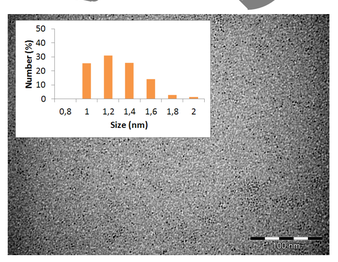



$Ru^0$@dppb-TS NPs
(1.0 ± 0.2 nm)

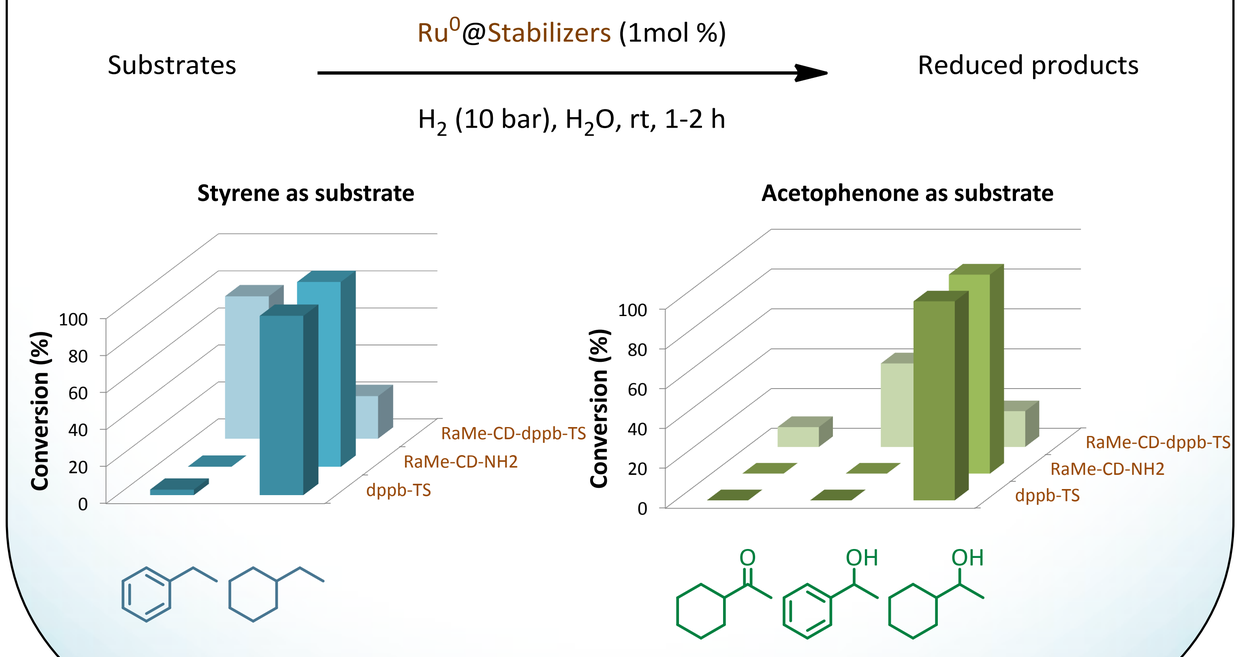



$Ru^0$@RaMe-CD-$NH_2$ NPs
(1.4 ± 0.2 nm)




$Ru^0$@RaMe-CD-dppb-TS NPs
(1.2 ± 0.3 nm)

### Reactivity of $Ru^0$@stabilizers NPs




## Conclusions – Perspectives

$Ru^0$ NPs were easily prepared and stabilized with various protective agents by two approaches: decomposition of metal salts (one-pot or cascade methods) and decomposition of organometallic complexes. TEM analyses confirmed the formation of small and well-dispersed NPs, which were successfully used in hydrogenation of model substrates.

Preliminary tests on asymmetric hydrogenation of prochiral compounds were obtained with no significant enantiomeric excess (< 5%). Further studies on the influence of supramolecular edifices on the enantiomeric selectivity of NPs are still going on.


CONTACT :

Prof. Alain Roucoux
Equipe Organométalliques, Matériaux et Catalyse
ENS Chimie de Rennes
alain.roucoux@ensc-rennes.fr