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# New P^O ligand grafted on periodically organised mesoporous silicas for one-pot bifunctionnal catalysis: Coupling of base catalysed Knoevenagel condensation with *in situ* Rh catalysed hydrogenation†

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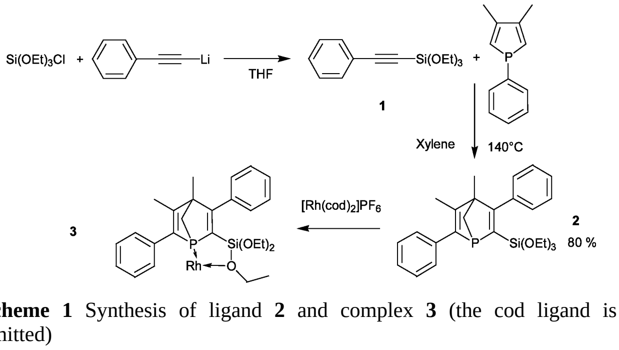
**The 1-phosphanorbornadiene-rhodium complex (Rh-PNBD) anchored on a mesostructured porous silica matrix is the first example of a rhodium center chelated by a phosphorus and an oxygen atom belonging to the anchoring siloxane moiety. These new hybrid silicas behave as very active recyclable hydrogenation catalysts, which combined with additional grafted amino functions allow efficiently driven one-pot bifunctionnal catalysis.**

During the last five years significant progress has been made in the field of "organised soft matter chemistry"[1,2] allowing controlled design of periodically organised mesoporous hybrid solids carrying inorganic, organic or even bio functionalities. Heterogenisation of organometallic catalysts through their anchoring on high surface inorganic materials is not only a way to facilitate their recycling, but also has an impact on their activity.[3–5] Moreover, covalent grafting of the catalytic entities also allows optimised synthetic procedures utilising complementary reagents which can be destructive to each other.[6] In metal based catalysis two main approaches were used to heterogenise organometallic complexes.[7] The first one, called supported homogeneous catalysis, uses large spacers to anchor the active complex in order to preserve the coordination sphere and mobility close to those of the homogeneous complex.[8] In the second approach, called heterogeneous molecular catalysis, the active complex is anchored *via* a direct bond with the inorganic surface.[5]

The present anchored 1-phosphanorbornadiene–Rh [Rh-PNBD@SiO$_2$] complex can be described as a new catalytic centre that combines conceptually supported homogeneous catalysis and heterogeneous molecular catalysis. The first synthesis step corresponded to the functionalisation of the PNBD[9] ligand with a triethoxysilyl group to allow the grafting of the complex (Scheme 1) to the silica surface. Therefore phenylethynyl lithium was reacted at room temperature in THF with triethoxy-silyl-chloride,[10] yielding 95% phenylacetyl-triethoxy-silane **1**. **1** was then heated at 140 °C in xylene with 1 equivalent of 1-phenyl-3,4-dimethyl-phosphol giving 1-phospha-2-triethoxysilyl-4,5-dimethyl-3,6-diphenyl-norbornadiene **2** (yield = 80%). (Scheme 1)

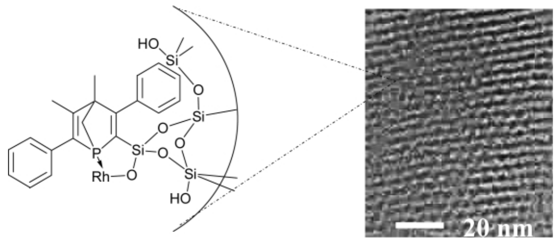


**Scheme 1** Synthesis of ligand **2** and complex **3** (the cod ligand is omitted)

In the presence of one equivalent of [Rh(acac)(CO)$_2$] the PNBD ligand **2** forms the hemi-labile P^O complex **3** as evidenced through NMR experiments ($\delta_p$ = 57.9 ppm, $^1J_{P-Rh}$ = 180 Hz). The three ethoxy groups of the triethoxysiloxane are magnetically equivalent, the $^1$H NMR signal of their CH$_2$ being a quadruplet of doublet ($\delta$ = 3.6 ppm, $^3J_{H-H}$ = 8.4 Hz, $^3J_{H-Rh}$ = 1.5 Hz). At −20 °C these latter signals begin to broaden suggesting that the recording temperature is close to the temperature of coalescence. Finally at −80 °C the exchange process is frozen as evidenced by the presence of a quadruplet integrating for 2 protons ($\delta$ = 3.4 ppm, $^3J_{H-H}$ = 6.5 Hz), and one multiplet ($\delta$ = 3.55 ppm) corresponding to the other ethoxy groups.

Two different mesoporous silicas where then used as catalytic supports. The first one synthesised as previously described[11] by sol–gel synthesis under acidic conditions in the presence of cetyltriethylammonuium bromide (CTEAB) as a surfactant yielding mesoporous silica with 750 m$^2$ g$^{-1}$ specific surface area, an average pore diameter of 23 Å and a cubic (*Pm*3*n*) pore structure organisation (as confirmed by N$_2$ adsorption isotherm and XRD experiments, respectively) (See supplementary material†). The second silica support was synthesized by standard SBA-15 type synthesis[12] and had a surface area of 630 m$^2$ g$^{-1}$, pore diameter of 60 Å and the pore structure is built following a hexagonal (*p*6*m*) arrangement (see TEM Scheme 2).

The PNBD ligand **2** was grafted on both silica based mesoporous materials, following previously described grafting procedures,[13] by stirring a suspension of 200 mg of the appropriate mesoporous silica (*Pm*3*n* or *p*6*m*) at 90 °C in toluene with 100 mg of **2** for 12 h. The resulting slightly yellow powders were extracted for 24 h with acetone in a soxhlet extractor. TGA analysis shows that 16.4 mass% of **2** were grafted on the *Pm*3*n* silica based material (**2@Pm3n**), whereas only 6.3 mass% of organic material were grafted on the *p*6*m* silica support (**2@p6m**). $^{31}$P MAS CP solid-state NMR measurements indicates that a small part of the phosphine is oxidised during the grafting, ($\delta$ = 57 ppm for PNBD with P=O and $\delta$ = −8 ppm for non-oxidised PNBD). However a large part of the compound remains unoxidised. When the corresponding PNBD grafted material is reacted with [Rh(acac)(CO)$_2$] (the Rh/PNBD ratio is 1 : 1) in CH$_2$Cl$_2$ for 30 min. and washed 3 times with CH$_2$Cl$_2$ the powder turns to pale orange. The corresponding materials are called **3@Pm3n** and **3@p6m**. In the



**Scheme 2** Supported complex **3**. The other ligands on the rhodium centre are omitted.

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† Electronic supplementary information (ESI) available: NMR spectra, TEM micrographs, N$_2$ adsorption/desorption isotherms. See http://www.rsc.org/suppdata/cc/b4/b403491k/

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FT-IR spectrum of this material, acetyl acetonate bands have disappeared whereas the signal of the carbonyl ligands are clearly visible (2002 and 2074 cm$^{-1}$) indicating that the grafted solid acts as a bidentate LX ligand toward the rhodium centre. This is confirmed by $^{31}$P MAS CP solid-state NMR measurements on **2@Pm3n** and **2@p6m** treated with [Rh(cod)$_2$]PF$_6$. A broad signal at 58 ppm in good agreement with the chemical shift of **3** and the fact that HPF$_6$ was washed away are consistent with the assumption that the solid acts as a P^O$^-$ ligand. This is, to the best of our knowledge, the first example of a complex including the metallic Rh centre in a five membered ring where the siloxane moiety of the ring is grafted on a silica surface (Scheme 2).

The catalytic activity of the grafted complexes towards hydrogenation of 1-hexene was tested under standard conditions (0.1 mol% of catalyst per run calculated on the basis of the rhodium precursor, in 20 ml MeOH, under 7 bars of H$_2$, at room temperature). As a control test, **2** was also grafted (8% in mass) on an amorphous silica gel (Geduran® Si 60 from Merck) yielding **2@SiO$_2$**. After impregnation of **2@SiO2** with the Rh precursor, the resulting catalytic material was labelled **3@SiO$_2$**. The main results concerning the Rh catalysed hydrogenation of 1-hexene are gathered in Table 1. After a given number of runs, the catalyst is isolated by filtration and washed before using it an additional time for hexene hydrogenation under the same conditions. This step corresponds to the recycling of the catalytic powder (Table 1). As the homogeneous catalyst **3** was inactive, we chose [Rh(cod)1-phospha-2-ethoxydimethylsilyl-3,6-diphenyl-4,5-dimethylnorbornadiene] **4** synthesised the same way as **3** as a reference. Kinetic studies of the 1-hexene hydrogenation catalysed by **4** showed that it is the hydrolysed complex **4′** which is active. In this case the PNBD derivate is a P^O$^-$ ligand corroborating the postulated structure of the grafted complex.

**3@Pm3n** and **3@p6m** proved to have a high activity and to be recyclable. It is interesting to point out that the **3@SiO2** (grafted on commercial amorphous silica gel) exhibited smaller turn over frequencies than **3@Pm3n** and **3@p6m** catalysts and did not exhibit any activity towards hexene hydrogenation after the first recycling. The difference of activity between **3@Pm3n** and **3@p6m** can be assigned to a better diffusion of reactants and products in the larger pores provided by the **3@Pm3n** mesoporous catalyst. (see Table 1)

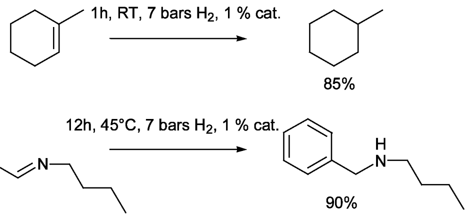
**3@p6m** was also tested on substrates, which are known to be more difficult to hydrogenate, namely 1-methyl-1-cyclohexen and an imine (Scheme 3). Regarding the smooth reaction conditions,[14] those results are, to the best of our knowledge, the best reported so far for hydrogenation of methylcyclohexene.

At this point, it was interesting to add a new functionality to our heterogeneous PNDB-silica based materials to test their potentiality as bifunctionnal catalysts. In the past decade much work has been done to catalyse Knoevenagel condensation in a heterogeneous way.[15] Therefore, an amino function was chosen to be added to **2@p6m** materials by grafting a well known silica coupling agent such as the aminopropyltriethoxysilane. Following the same methodology as the one described above,[13] a new catalyst labelled **[2+N]@p6m** with additional 14 mass% of amino compound was obtained. A rough calculation yields a ratio of 1 phosphanorbornadiene for 10 amino groups tethered on the surface as confirmed by elemental chemical analysis (N 2.3, P 0.15%) the corresponding Rh loaded material was labelled **[3+N]@p6m**, and this catalyst was used in the one-pot reaction described in Scheme 4. The reaction proceeded in two steps, 1 hour under argon allowing the Knoevenagel condensation to occur and then 12 hours under 7 bars hydrogen for the reduction. This latter approach conceptually opens new possibilities in the search for innovative polyfunctional catalysts.

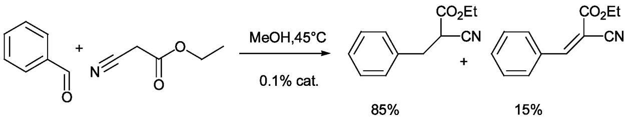
**Table 1** Hydrogenation of 1-hexene with grafted Rh catalyst

| Run | Catalyst | TOF$^a$ | Number of recyclings | TON$^b$ |
|---|---|---|---|---|
| 0 | **3** | 0 | X | 0 |
| 1 | **4′** | 7 | X | 1000 |
| 2 | **3@SiO$_2$** | 15 | 0 | 1000 |
| 3 | **3@pm3n** | 48 | 3 | > 100000 |
| 4 | **3@p6m** | 72 | 2 | 5600 |

$^a$ Turn over frequency in cycle min$^{-1}$. $^b$ Turn over number molar ratio between the amount of hexene converted and the amount of catalyst.



**Scheme 3** Hydrogenations with **3@p6m**



**Scheme 4** One-pot Knoevenagel condensation followed by reduction on **[3+N]@p6m**

## Notes and references

1 S. Mann, S. L. Burkett, S. A. Davis, C. E. Fowler, N. H. Mendelson, S. D. Sims, D. Walsh and N. T. Whilton, *Chem. Mater.*, 1997, **9**, 2300.
2 G. J. de A. A. Soler-Illia, C. Sanchez, B. Lebeau and J. Patarin, *Chem. Rev.*, 2002, **102**, 4093.
3 A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
4 R. Anwander, *Chem. Mater.*, 2001, **13**, 4419.
5 C. Copéret, M. Chabanas, R. Petroff Saint-Arroman and J.-M. Basset, *Angew. Chem. Int. Ed.*, 2003, **42**, 156.
6 F. Gelman, J. Blum and D. Avnir, *J. Am. Chem. Soc.*, 2000, **122**, 11999.
7 A. Choplin and F. Quignard, *Coord. Chem. Rev.*, 1998, **178–180**, 1679.
8 For example see: C. M. Crudden, D. Allen, M. D. Mikoluk and J. Sun, *Chem. Commun.*, 2001, 1154.
9 F. Mathey, F. Mercier, C. Charrier, J. Fischer and A. Mitschler, *J. Am. Chem. Soc.*, 1981, **103**, 4595.
10 Adapted from: H. W. Post and H. M. Norton, *J. Org. Chem.*, 1942, **7**, 528.
11 Adapted from: V. Goletto, V. Dary and F. Babonneau, *Mater. Res. Soc. Symp. Proc.*, 1999, **576**.
12 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
13 D. Brunel, A. Cauvel. F. Di Renzo, F. Fajula, B. Fubini, B. Onida and E. Garrone, *New J. Chem.*, 2000, **24**, 807.
14 Compare with A. Zsigmond, K. Bogar and F. Notheisz, *J. Catal.*, 2003, **213**, 103.
15 D. J. Macquarrie, J. H. Clark, A. Lambert, J. E. G. Mdoe and A. Priest, *React. Polym.*, 1997, **35**, 153.