

## Influence of organic ligands on the stabilization of palladium nanoparticles

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### Abstract

The synthesis of palladium nanoparticles is performed by hydrogenation of a precursor, Pd<sub>2</sub>(dba)<sub>3</sub> (**1**) or [Pd(C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> (**2**) in the presence of either a weakly coordinating ligand (hexadecylamine, HDA) or good ligands (polyphosphines). It is shown in the case of **1** that good ligands lead to stable spherical nanoparticles of small size (near 2 nm) whereas the protective effect of HDA depends on the amount of ligand added as a result of equilibria present at the surface of the particles as monitored by solution NMR spectroscopy. The decomposition of **2** being very fast, the particle growth cannot be controlled except in the case of the use of a large excess of HDA which leads to spongelike particles resulting from the agglomeration of initially obtained nanocrystallites.

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### 1. Introduction

The chemistry and catalytic properties of colloids have attracted an ever increasing interest for the past 10 years [1–6]. The catalytic properties of these particles for hydrogenation reactions, in particular of arenes, have been widely recognized and their use for other reactions such as C–C coupling is rapidly developing [7–9]. In this respect, the last period has evidenced the importance of the understanding of the surface organometallic chemistry of these nanoparticles. This has led to consider that nanoparticles are very large organometallic objects and therefore to study ligand coordination and mobility at their surface [10,11].

However, while the chemistry of metal nanoparticles is attracting more and more attention, a number of questions become recurrent. They concern: (i) the way to control the monodispersity of the particles; (ii) the way to control their shape; (iii) the surface state of the particles, or, in other words the nature of the surface ligands or contaminants. In addition, a fourth question, probably the most difficult one, concerns the fate of the particles in solution, namely change of size, shape, interchange between the colloidal and the molecular state and hence the nature of the active species for reactions catalyzed by such species in solution [12–15].

Concerning points (i) and (ii), high temperature methods using surfactants have been developed for III–V and II–VI semi-conductors and adapted for magnetic metals while, more recently, an organometallic approach was developed in our group. However, besides gold and silver, less effort has been devoted to the

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synthesis of monodisperse noble metal nanoparticles and to the control of their shape. This is of course a result of the interest of the researchers for their chemical properties rather than for their physical properties which are very dependent upon particles shape and organization. The question of the size dependence of the catalytic properties of palladium nanoparticles has however been recently addressed by El-Sayed and coworkers [16].

As far as noble metals are concerned, the common methods to stabilize the nanoparticles and control their growth is to use polymers [17–19] or ligands. These ligands may be relatively traditional (thiols [20–22], amines [23–25], phosphines [26–28], phenantroline [29,30]) or more unusual such as the polyoxo anions used by Finke and coworkers [31,32] or the fluoros ligands employed by Moreno-Mañas et al. [33,34]. However, while it is well-known that the ligands will be determinant for inducing a specific reactivity to molecular complexes, little is known on the role of the ligands when coordinated to the surface of nanoparticles. In addition, it is frequently difficult to compare the synthetic methods used by different research groups due to the different nanoparticles generation methods (salt reduction, decomposition of organometallic precursors but then, role of the ligands initially present on the precursors, metal vapour synthesis, etc.). In the past few years, we have studied the coordination properties of different ligands on metal nanoparticles [17,23,24,35–39]. For example, we have demonstrated that while thiols are firmly fixed on the surface of ruthenium [24] and platinum [17] nanoparticles, amines would undergo in solution a rapid exchange process at the NMR time scale between free and coordinated ligands. We have also recently shown that palladium nanoparticles stabilized by a chiral diphosphite were slow but selective catalysts for an asymmetric allylic alkylation reaction [40]. It is well-known that palladium is a difficult problem since molecular complexes of this element show a strong tendency to precipitate when used as homogeneous catalysts whereas there is some evidence for nanoparticles corrosion when used as colloidal catalysts. Different methods were recently reported to prepare and stabilize palladium nanoparticles including one derived from the semi-conducting nanoparticles synthesis [16,20,26,28,33,34,41–46].

This led us to start a systematic study on the synthesis of palladium nanoparticles in different conditions from different precursors and to follow their reactivity in solution. Our results are here reported.

## 2. Results

The reactions were carried out, as a standard procedure, in a Fischer–Porter bottle, at room temperature, under three bars of dihydrogen for 20 h. In order to determine the importance of reaction conditions on

the control of the particles syntheses, three parameters were evaluated namely nature of the precursor, nature of the ligands and nature of the solvent. Either  $\text{Pd}_2(\text{dba})_3$  (**1**) or  $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$  (**2**) were used as palladium precursors. One of these complexes ( $\text{Pd}_2(\text{dba})_3$  (**1**)) decomposes relatively slowly but potentially keeping some of its initially coordinated ligands (or their derivatives), while complex (**2**) ( $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ ) decomposes rapidly without leaving any reactive residue. Concerning the solvents, both a coordinating one, THF, and a non-coordinating one, toluene, have been chosen. Finally, a weakly coordinating ligand (hexadecylamine, HDA) and good ligands such as polyphosphines have been tested.

The reaction of **1** (150 mg; 0.16 mmol) with  $\text{H}_2$  in 40 ml THF is very dependent upon the concentration of HDA present in the reaction medium. In all cases, we have demonstrated that the dba ligand initially present in the complex was hydrogenated and easily removed from the particle surface by washing with organic solvents such as pentane. In the presence of 0.1 eq. of  $[\text{HDA}]/[\text{Pd}]$ , particles agglomerated with no defined shape were obtained. The particles show a better separation and an elongated shape when 1 eq. HDA is present. When using 10 eq. HDA, the particles are well separated and display a spherical shape, a mean size near 6 nm and relatively low size dispersity (Fig. 1). This tendency, namely the better stabilization induced by larger amounts of ligands, is even more pronounced when using dilute solutions. Changing from a coordinating solvent such as THF, previously demonstrated to participate to the stabilization of Pt nanoparticles [36], to a non-coordinating solvent such as toluene leads to severely agglomerated particles when using 0.1 eq. HDA, to less agglomerated but elongated particles using 1 eq. HDA and to particles not very different from those obtained in THF although with a higher aspect ratio, when using 10 eq. HDA (Fig. 2).

If the reactions are carried out using the alternative precursor **2** in THF concentrated conditions, no stabilization is achieved upon using 0.1 or 1 eq. HDA and the formation of “spongelike” particles when using 10 eq. HDA is observed (Fig. 3). These particles result from the agglomeration of nanocrystallites. Precedents for this type of particles have been observed in the chemistry of ruthenium [47,48] and that of platinum [49]. They usually result from the poor stabilization of the initially formed nanoparticles by the surrounding medium and ligands. Since these experiments did not lead to satisfactory results in terms of formation of individual particles, we have not pursued the full characterization of these agglomerated particles and in particular the role of the chloride groups in their formation and stabilization.

All the WAXS measurements performed on this series of nanoparticles revealed well-crystallized Pd nano-

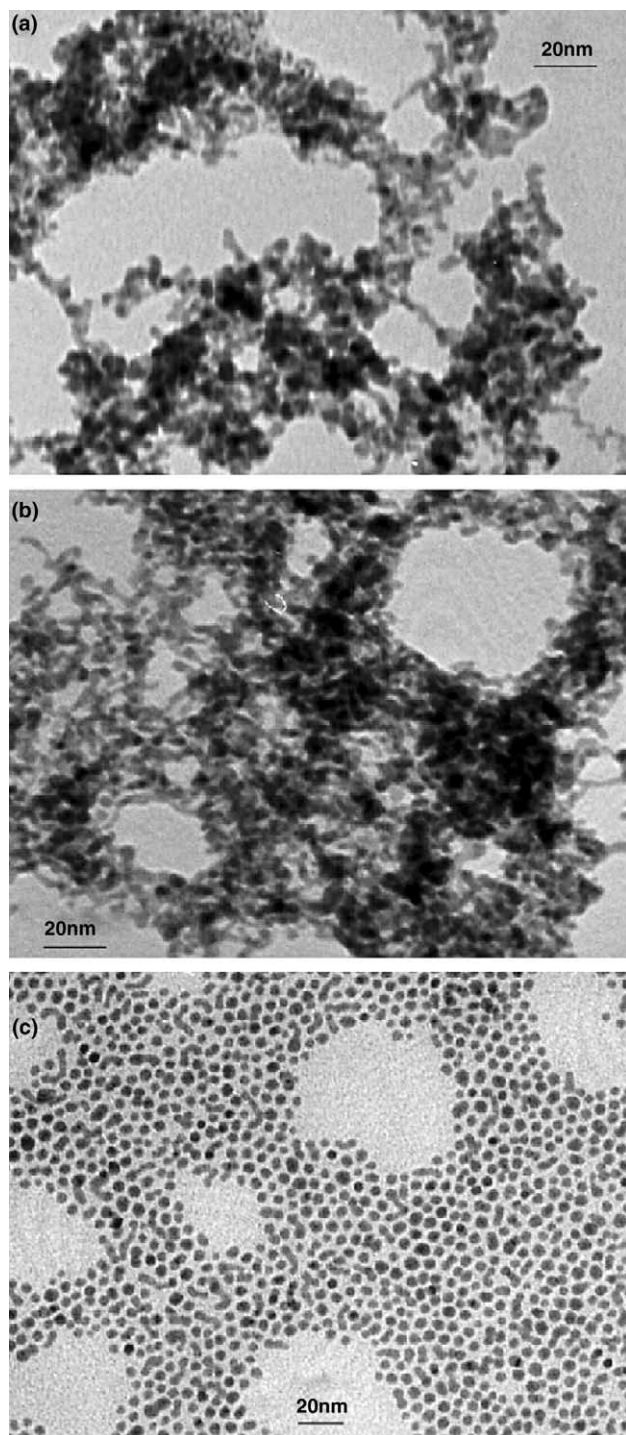


Fig. 1. TEM micrographs of Pd nanoparticles synthesised in THF from  $\text{Pd}_2(\text{dba})_3$  and in the presence of: (a) 0.1 eq. HDA/Pd; (b) 1 eq. HDA/Pd; (c) 10 eq. HDA/Pd.

particles displaying a fcc structure and a coherence length comprised between 3.5 and 5.0 nm (Fig. 4).

The IR spectrum of Pd/0.1 eq. HDA particles synthesised in THF (Fig. 5), recorded on a crude concentrated solution shows bands at 3327 and 2845–2950  $\text{cm}^{-1}$  corresponding to N–H and C–H stretching bands, thus

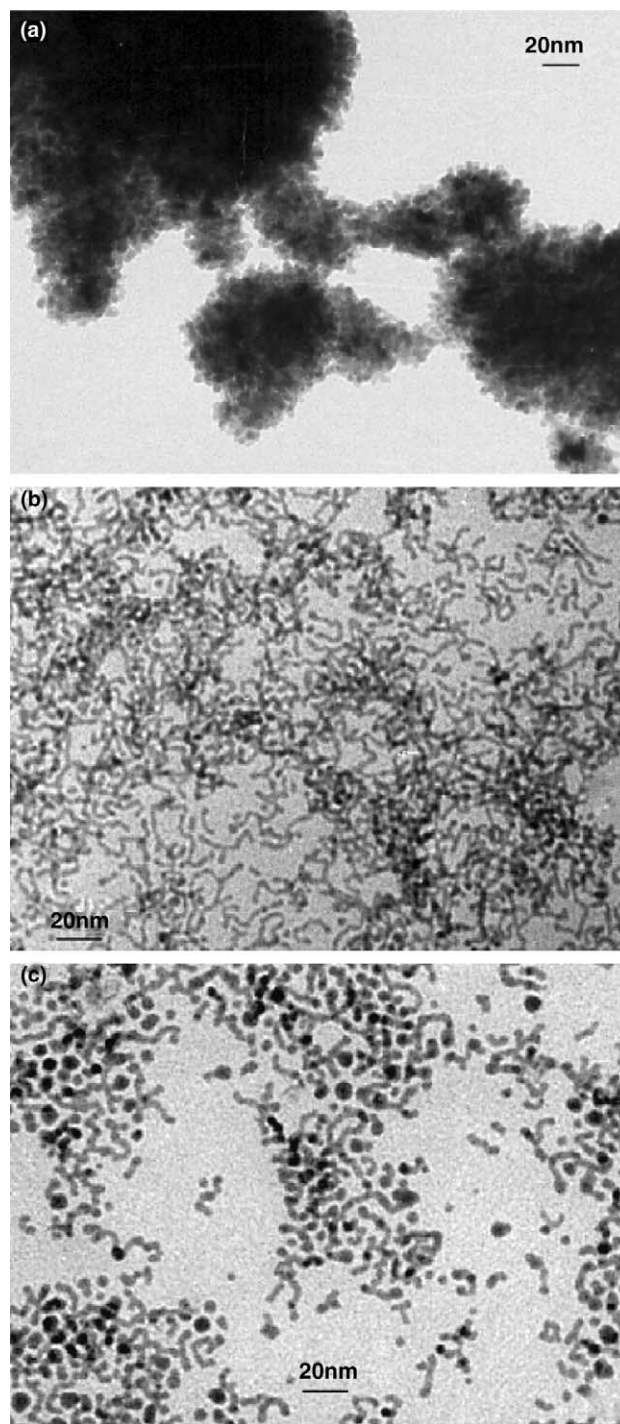


Fig. 2. TEM micrographs of Pd nanoparticles synthesised in toluene from  $\text{Pd}_2(\text{dba})_3$  and in the presence of: (a) 0.1 eq. HDA/Pd; (b) 1 eq. HDA/Pd; (c) 10 eq. HDA/Pd.

confirming the presence of amine ligands near the surface of the particles. However, other bands were observed which could be attributed to dba, arising from the Pd precursor, or to some of its derivatives. A strong band is visible at 1706  $\text{cm}^{-1}$ , shifted at high frequency compared to the C=O stretch of the dba carbonyl group

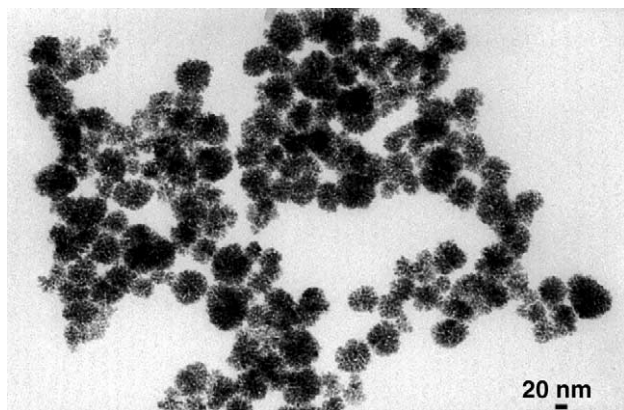


Fig. 3. TEM micrograph of spongelike Pd nanoparticles synthesised in THF from  $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$  in the presence of 10 eq. HDA/Pd.

expected near  $1652\text{ cm}^{-1}$ . In addition, the characteristic bands of the alkene moieties are missing. These data are in favour of the hydrogenation of the  $\text{CH}=\text{CH}$  bonds of dba in the particles synthesis conditions, hence producing 1,5-diphenyl-3-pentanone. We do not know if this ketone is initially coordinated on the particles surface or only present in the close environment of the particles. It is however easily removed from the colloids by washing with pentane. Thus, a spectrum of particles synthesized in the presence of 10 eq. of HDA recorded before purification shows the presence of ketone derivatives (presence of a band at  $1718\text{ cm}^{-1}$  characteristic of a  $\text{C}=\text{O}$  group) and HDA ligands. The observed ketone is again not dba but its hydrogenated derivative assumed to be 1,5-diphenyl-3-pentanone. An IR spectrum recorded after purification of this colloid by addition of pentane, appears very similar to that of pure HDA. We do not observe any band between  $1650$  and  $1710\text{ cm}^{-1}$  which could be attributed to carbonyl groups. The purification step has then led to the elimination of the dba hydrogenation product but not of HDA.

NMR experiments have also been carried out in solution on Pd nanoparticles stabilized by 10 eq. HDA ( $^1\text{H}$  NMR at 400 MHz and  $^{13}\text{C}$  NMR at 101 MHz in  $\text{THF-d}^8$ , 300 K). As first experiments,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Fig. 6) have been recorded on crude Pd/10 eq. HDA nanoparticles obtained by evaporation of the reaction mixture without any purification step and further dissolution in  $\text{THF-d}^8$ . Under these conditions, signals corresponding to the different atoms of the alkyl chain of the amine are observed together with other signals which can be attributed in one hand to a dba hydrogenation product (1,5-diphenyl-3-pentanone) and in another hand to a new product, presumably an imine, resulting from a condensation reaction between dba and HDA. Sharp peaks corresponding to the methyl and methylene carbons of HDA are clearly visible, respectively, at 14 (C16), 23 (C15), 30 (C4–C13) and 32 (C14) ppm. In addition, the resonances at 42.8, 34.6 and 27.4 ppm

and corresponding to the carbons in positions C1, C2 and C3, close to the amine function are broad. Upon washing the same colloid with pentane, only a few signals remain on the  $^{13}\text{C}$  NMR spectrum, namely at 14 (C16), 23 (C15), 30 (C4–C13) and 32 (C14) ppm. The C1–C3 carbons of HDA are not visible, nor are the signals of the hydrogenation product of dba. This demonstrates the elimination through purification of dba as well as excess free HDA. The absence of observation of C1–C3 carbons is due to the coordination of HDA at the surface of the particles and to the slow tumbling of the colloid in the THF solution. The appearance of these peaks as broad resonances in the presence of excess HDA results from a fast exchange at the NMR time scale between free and coordinated HDA as previously observed for HDA protected ruthenium nanoparticles. [24]. If a large excess of HDA is further added, all peaks of HDA are visible which confirms the presence of such an exchange. In a similar way, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of a crude unpurified colloid consisting of palladium nanoparticles stabilized by 0.1 eq. HDA has been recorded. In this case, and as previously noticed for Pd/10 eq. HDA nanoparticles, we observe the signals of the HDA alkyl chain except those corresponding to carbons C1–C3. This again results from the coordination of HDA at the surface of the particles. In addition, we can observe that the dba ligands of the Pd precursor have been hydrogenated and that a condensation product has been formed.

In order to obtain a better stabilization of the particles, we changed ligands and used phosphines. Preliminary experiments regarding the use of  $\text{PPh}_3$  as a stabilizing ligand for palladium nanoparticles have evidenced the need for the presence of some excess phosphine to stabilize the particles which in turn led to some problems regarding the dissolution of palladium in the organic solvents present. We therefore used polyphosphines for the stabilization of the particles. Two ligands were chosen, namely a diphosphine, bis(diphenylphosphino)decane, (**a**) and a triphosphine, bis(diphenylphosphinoethyl)-phenylphosphine, (**b**).

The reactions were carried out in THF in the presence of 0.2 eq. of the ligands **a** or **b**, in similar conditions to those previously described here-above, but using dilute conditions (standard conditions: 0.172 mmol [Pd] in 80 ml THF and 0.034 mmol ligand). In contrast to the reactions carried out using HDA as stabilizing ligand, we obtained in each case very small and spherical nanoparticles. These particles are well dispersed although sometimes embedded in large agglomerates, probably because of the presence of excess ligand (Fig. 7). The sizes of the particles were found to be near 1.6 nm for ligand (**a**), and near 2.7 nm for ligand (**b**). Diluting or concentrating the solution while keeping constant the  $[\text{ligand}]/[\text{Pd}]$  ratio had no effect on the particles size and their dispersion.

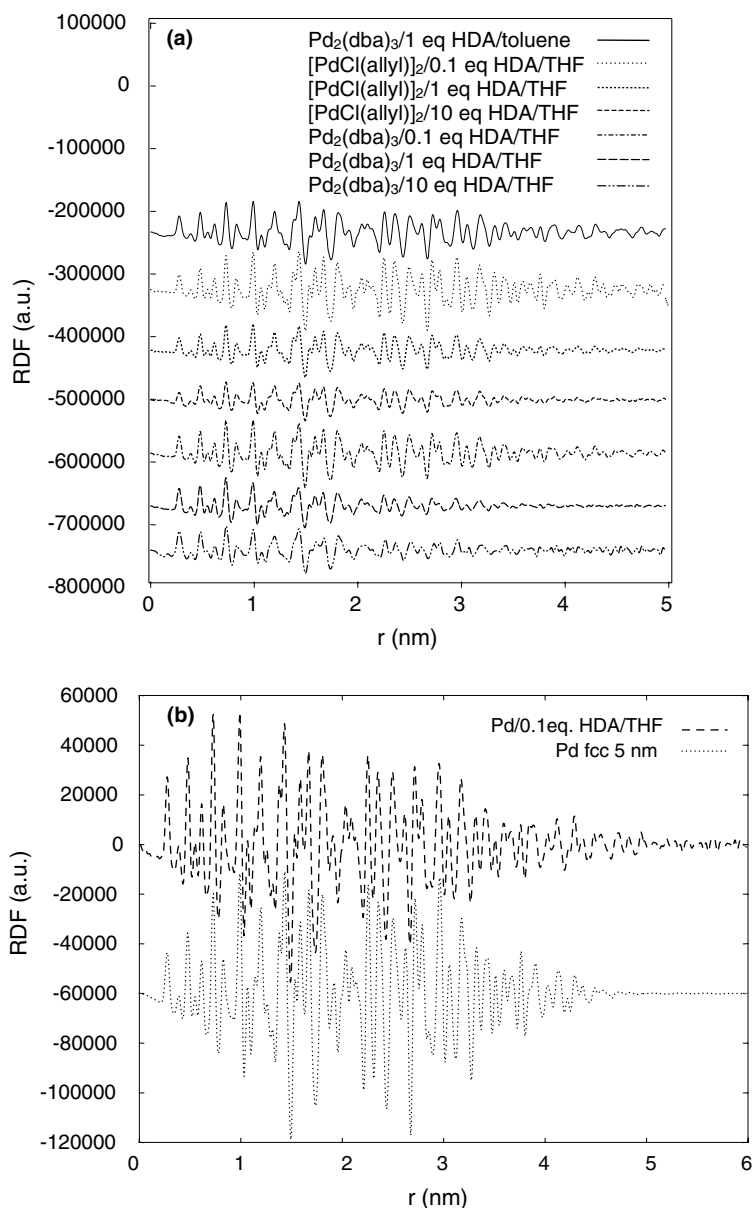


Fig. 4. (a) WAXS measurements on Pd/HDA nanoparticles. (b) Comparison between experimental rdf obtained for Pd/0.1 eq. HDA nanoparticles synthesised in THF (top) and theoretical rdf for Pd fcc 5 nm nanoparticles (bottom).

WAXS experiments evidence the crystalline state of the nanoparticles and their fcc structure (Fig. 8). The coherence length is estimated to, respectively, ca. 2 and 3.5 nm for the Pd nanoparticles stabilized by ligands (a) and (b). It is in good agreement with the TEM sizes (respectively, 1.6 and 2.75 nm). In addition, the Pd nanoparticles stabilized by (a) appear not very crystalline but disordered.

The WAXS data do not reveal the presence of molecular species in addition to the nanoparticles. The particles were obtained as powders after precipitation and washings with pentane. They were found stable, both in solution and in the solid state and did not show any sign of evolution with time.

### 3. Discussion

We have previously reported the synthesis of platinum nanoparticles [17] stabilized by thiol ligands and that of ruthenium nanoparticles [24] stabilized either by thiols or by amines. We have found that thiols would firmly coordinate to the surface of the particles and would not undergo exchange with free thiol ligands in solution whereas it was exactly the contrary for ruthenium particles stabilized by amines on which a fast exchange between free and coordinated amine was observed at the NMR time scale in THF. Here, we see a phenomenon of this type, namely the fast exchange between free and coordinated amine ligands to the surface

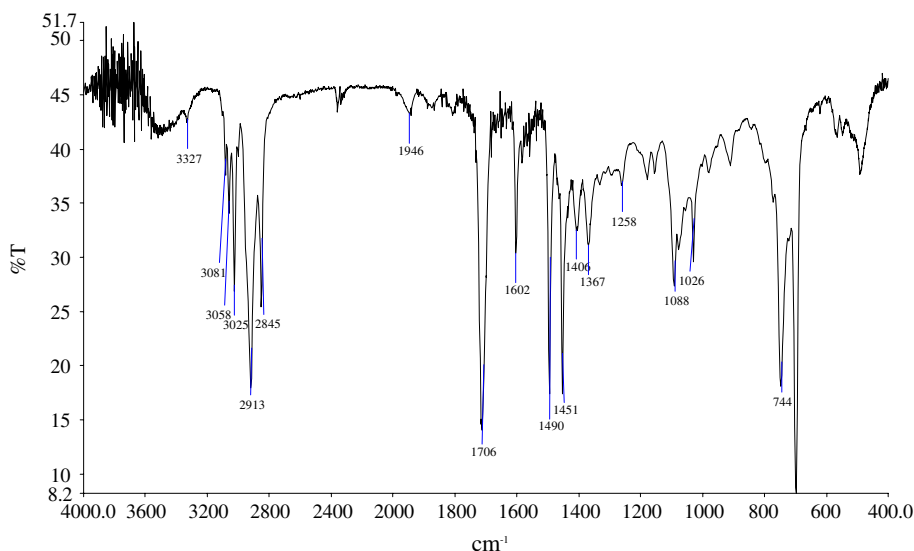


Fig. 5. IR spectrum recorded on a crude concentrated solution of Pd/0.1 eq. HDA nanoparticles in THF.

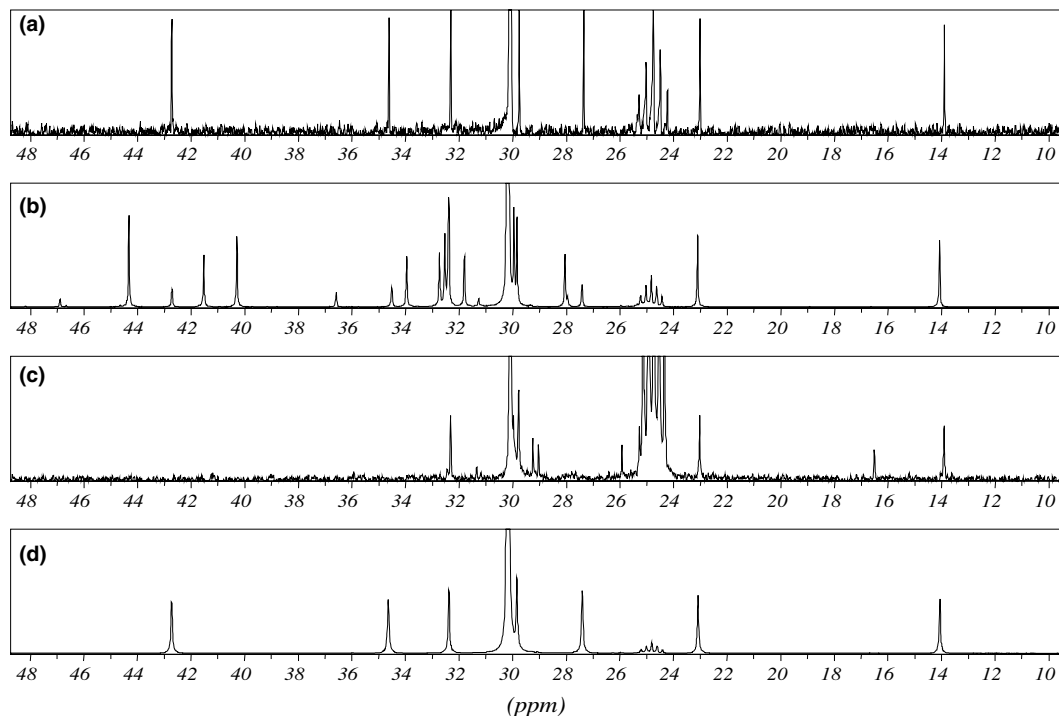


Fig. 6.  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (101 MHz) solution studies in  $\text{THF-d}^8$ : (a) pure HDA; (b) Pd/10 eq. HDA nanoparticles; (c) Pd/10 eq. HDA nanoparticles after purification by pentane; (d) Pd/10 eq. HDA nanoparticles after purification and addition of 0.5 eq. HDA in the NMR tube.

of palladium particles. This suggests that amines are generally weakly coordinated to platinum metal nanoparticles and that they can be easily displaced from their surface.

In this study, we use two precursors, one, (**2**), which decomposes very rapidly and the other, (**1**), which releases more slowly the Pd atoms through hydrogenation of dba into 1,5-diphenyl-3-pentanone and condensation of some of it with HDA into presumably an imine which

was not characterized. The kinetic of the decomposition reaction of **1** is slower than that of **2** and leads to potential weak ligands of the surface of the nanoparticles (dba or derivatives resulting from its hydrogenation or a condensation reaction). Using **2**, no stabilization of the particles is achieved, at low amine contents. Only with 10 eq. amine do we get some “spongelike” particles. In contrast, using **1** as a precursor, the stabilization depends upon the amount of amine and the solvent. If the reac-

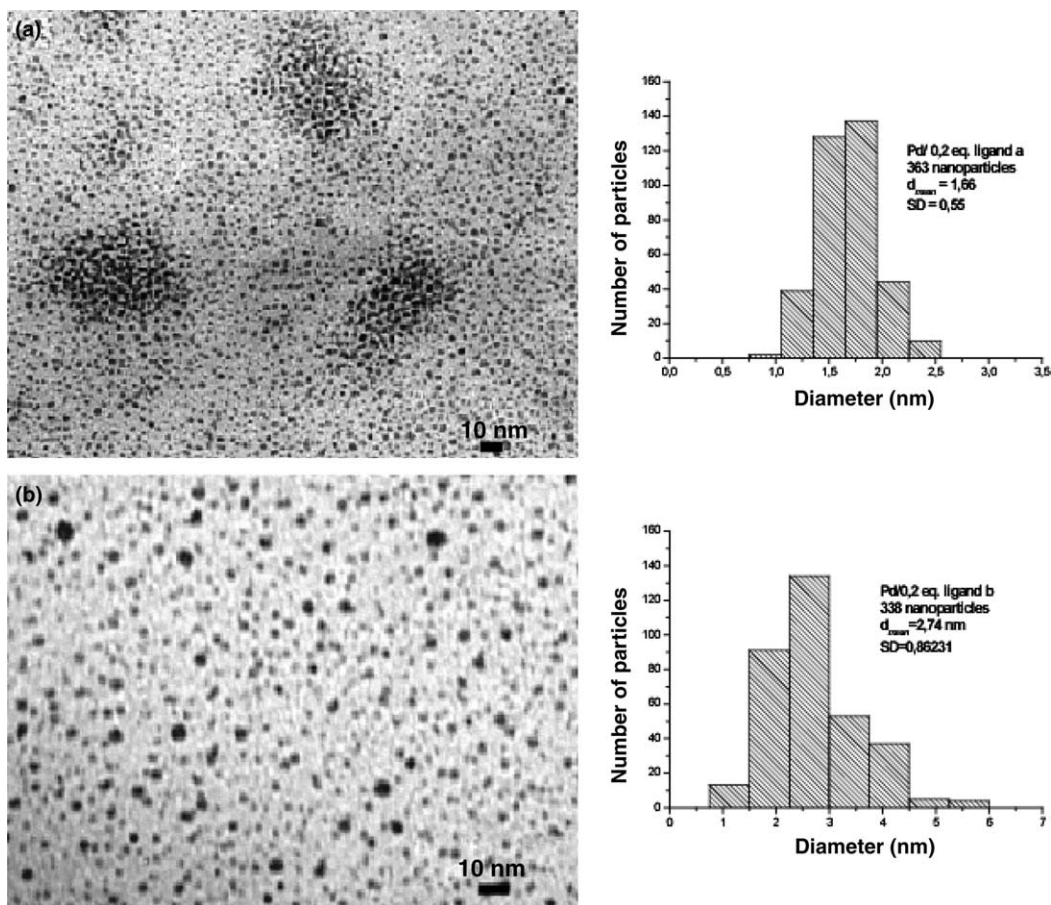


Fig. 7. TEM micrographs of Pd nanoparticles synthesised in THF from  $\text{Pd}_2(\text{dba})_3$  and in the presence of: (a) 0.2 eq. **a**/Pd; (b) 0.2 eq. **b**/Pd.

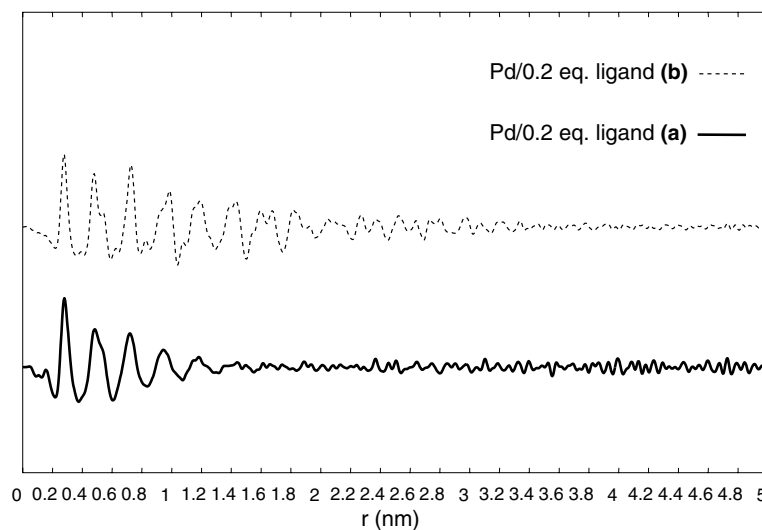


Fig. 8. WAXS measurements on Pd/0.2 eq. phosphine stabilized nanoparticles.

tion is carried out in a non-coordinating solvent, toluene, no stabilization is achieved using 0.1 eq. HDA while long and regular noodle-like particles form in the presence of 1 eq. HDA and separated but not spherical par-

ticles in the presence of 10 eq. HDA. If another stabilizing agent is added, the solvent THF, then particles of the same type (elongated-coalesced) are observed for 0.1 and 1 eq. HDA whereas well-separated spherical

nanoparticles of 6 nm mean size are formed in the presence of 10 eq. HDA. This series of experiments demonstrates the predominant role of chemical equilibria between all potential coordinating agents (ligands resulting from the precursor, solvent and amine) for stabilizing the nanoparticles. Only in the presence of a large excess of ligands are spherical nanoparticles obtained. Upon decreasing the amine content or substituting THF for toluene, coalescence becomes possible and leads to particles of elongated shapes, the most regular ones being those obtained in toluene in the presence of 1 eq. HDA. This suggests that HDA is organized in this medium and that the coalescence of the particles occurs in channels created by this organization. Similar effects have been observed with ruthenium and nickel nanoparticles [24,38].

In contrast to these observations, no such size and shape changes or solvent dependence is observed when using the polyphosphine ligands. This demonstrates that these ligands are firmly coordinated at the surface of the particles and suggest that the size observed results from a kinetic control of the growth process. Particles of very small size (ca. 1.6 nm) are obtained when using the bis(diphenylphosphino)decane (**a**) ligands, perhaps as a result of their easy adaptation (chain flexibility) to the surface of the particles. In addition, the ligand (**a**) stabilized nanoparticles are sometimes embedded into large organizations resulting from interaction of the ligands between two particles. The fact that no agglomeration and coalescence are observed implies that the polyphosphine ligands are chelating the nanoparticles surface. In addition,  $^{31}\text{P}$  NMR solution experiments clearly evidenced the absence of any phosphorus signal and, as a consequence, the absence of ligand exchange processes. These results are in agreement with a strong coordination of the polyphosphines at the surface of the particles. These are therefore good ligands for the study of individual properties of the particles.

In conclusion, the size and shape of nanoparticles can be modified according to the nature of the stabilizing ligands and, in the case of a weak ligand such as an amine, by the quantity of ligand added which controls the equilibria present at the surface of the particles. The process of ligands exchange and particles coalescence occurs in very mild conditions and can be controlled in the case of a difficult metal such as palladium, using common methods of organometallic chemistry.

## 4. Experimental

### 4.1. General procedure and reagents

All manipulations were carried out under argon using standard Schlenk tube or Fischer–Porter bottle and vacuum line techniques, or in a glove-box.

$\text{Pd}_2(\text{dba})_3$  and  $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$  were purchased from Strem Chemicals, Hexadecylamine (HDA; 99%) from Fluka and TRIPHOS (ligand **b**) from Aldrich.  $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$  [Y. Tatsuno, T. Yoshida, S. Otsuka, Inorg. Synth. 28 (1990) 342] and ligand **a** were synthesized following methodologies previously described. [T.-S. Chou, C.-H. Tsao, S.C. Hung, J. Org. Chem. 50 (1985) 4329–4332].

Solvents were purchased from SDS and dried and distilled prior to use: THF over sodium/benzophenone, toluene over sodium and pentane over calcium hydride. THF- $\text{d}^8$  (SDS, 99.5%) was dried over activated 4 Å molecular sieves.

All reagents and solvents were degassed before use by using three freeze-pump-thaw cycles.

### 4.2. Synthesis of Pd/HDA nanoparticles from the precursor $\text{Pd}_2(\text{dba})_3$

150 mg of  $\text{Pd}_2(\text{dba})_3$  (0.16 mmol) and the chosen quantity of HDA (7.9 mg for 0.1 eq. HDA/Pd; 79 mg for 1 eq. HDA/Pd and 790 mg for 10 eq. HDA/Pd) were dissolved in a Fischer–Porter bottle under argon at room temperature in THF or toluene under vigorous stirring. The mixture has then been pressurised under dihydrogen (3 bars). The colour of the solution turned from purple to black. The hydrogen pressure and the temperature were maintained for 20 h. After that period of time, the colloidal solution is black and homogeneous. A drop of each crude colloidal solution was deposited under argon on a holey carbon covered copper grid for TEM analysis. The colloidal solution was then concentrated to ca. 5 ml. Addition of cold pentane (20 ml) allowed the precipitation of the particles as black solids which were washed with pentane ( $3 \times 20$  ml) and dried under reduced pressure.

The same procedure has been followed for the reactions carried out in dilute conditions except the reagents quantities which were adapted to a precursor quantity of 40 mg (0.087 mmol).

### 4.3. Synthesis of Pd/HDA nanoparticles from the precursor $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$

150 mg of  $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$  (0.82 mmol) and the chosen quantity of HDA (20.3 mg for 0.1 eq. HDA/Pd; 199 mg for 0.1 eq. HDA/Pd and 1.98 g for 10 eq. HDA/Pd) were dissolved in a Fischer–Porter bottle under argon at room temperature in THF under vigorous stirring. The mixture has then been pressurised under dihydrogen (three bars). The colour of the solution turned in a few minutes from yellow to dark grey. The hydrogen pressure and the temperature were maintained for 20 h. After that period of time, the colloidal solution is dark grey and a precipitate is formed. A drop of each crude colloidal solution was deposited under argon on a holey carbon covered



copper grid for TEM analysis. The colloidal solution was then concentrated to ca. 5 ml. Addition of cold pentane (20 ml) allowed the total precipitation of the particles as black solids which were washed with pentane ( $3 \times 20$  ml) and dried under reduced pressure.

#### 4.4. Synthesis of Pd/polyphosphines nanoparticles from the precursor $Pd_2(dba)_3$

80 mg of  $Pd_2(dba)_3$  (0.086 mmol) were dissolved in a Fischer–Porter bottle under argon at  $-10$  °C in a THF solution containing 0.034 mmol of the chosen phosphine ligand (17.3 mg for **a**; 18.1 mg for **b**) under vigorous stirring. The mixture has then been pressurised under dihydrogen (three bars) at room temperature. The colour of the solution turned from red to grey in a few minutes. The hydrogen pressure and the temperature were maintained for 20 h. After that period of time, the colloidal solution appears as a black suspension. A drop of each crude colloidal solution was deposited under argon on a holey carbon covered copper grid for TEM analysis. The colloidal solution was then concentrated to ca. 5 ml. Addition of cold pentane (20 ml) allowed the precipitation of the particles as black solids which were washed with pentane ( $3 \times 20$  ml) and dried under reduced pressure.

## 5. Characterization

### 5.1. TEM Analysis

Samples for TEM analysis were prepared in a glove-box by slow evaporation of a drop of the colloidal solution deposited onto a carbon-covered copper grid. TEM analysis were performed at the “Service Commun de Microscopie Electronique de l’Université Paul Sabatier” (TEMSCAN) on a JEOL 200 CX-T electron microscope operating at 200 kV with a point resolution of 4.5 Å. The size distributions were determined through a manual analysis of enlarged micrographs by measuring ca. 300 particles on a given grid to obtain a statistically size distribution and a mean diameter.

### 5.2. WAXS analysis

Wide-angle X-ray scattering was performed at the CEMES-CNRS. All samples were sealed in 1 mm-diameter Lindemann glass capillaries. The measurements of the X-ray intensity scattered by the samples irradiated with graphite-monochromatized Mo  $K\alpha$  (0.071069 nm) radiation were performed using a dedicated two-axis diffractometer. Radial distribution functions (RDF) were obtained after Fourier Transformation of the reduced intensity functions.

### 5.3. IR analysis

IR spectra were recorded on a Perkin–Elmer Spectrometer GX (FT-IR). The samples have been prepared by deposition of a drop of concentrated solution onto KBr pellets.

### 5.4. NMR investigations

Solution NMR experiments were performed on a Bruker AMX 400 spectrometer (resonance frequencies of 400 MHz for  $^1H$  and 101 MHz for  $^{13}C$ ). The particles were dispersed in THF- $d^8$  under argon.

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