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The Preparation of Palladium Nanoparticles

Controlled particle sizes are key to producing more effective and efficient materials

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Palladium nanoparticles are of great importance as catalytic materials, as well as for a number of other applications such as hydrogen storage and sensing. Their synthesis has been widely studied and interest in their properties is growing. Here the synthesis of palladium nanoparticles by chemical and electrochemical methods using a variety of stabilisers including organic ligands, salts/surfactants, polymers and dendrimers is reviewed and their potential benefits in catalytic applications are introduced.

1. Introduction

Nanotechnology represents one of the major breakthroughs of modern science, enabling materials of distinctive size, structure and composition to be formed. Such nanodimensional materials (in the 1–100 nm size domain) are seen as a bridge between atomic and bulk materials and have been shown to exhibit a variety of unique chemical, physical and electronic properties (1). The study of these properties has become an increasingly important area in chemistry, physics, biology, medicine, and material sciences. However, reliable preparations of the nanomaterials are required for their exploitation, and this remains an area of active research.

Whilst much research has focussed on nanomaterials of the coinage metals (especially those of gold) (2), interest in the properties of other transition metal nanomaterials is also considerable and growing (3). The high surface-area-to-volume ratio makes nanomaterials highly desirable for use as potential catalysts. Given that palladium is one of the most efficient metals in catalysis (4, 5), the study of palladium-based materials is hugely important and valuable. As a consequence, nanoparticles of palladium have been heavily studied in a wide range of catalytic applications including hydrogenations (6, 7), oxidations (8, 9), carbon–carbon bond formation (10, 11), and electrochemical reactions in fuel cells (12). However, it should be noted that the applications of palladium go beyond catalysis. For example, the propensity of palladium to adsorb hydrogen has also led to palladium nanoparticles being utilised in hydrogen storage (13, 14) and sensing applications (15, 16).

In the present article, the synthesis of palladium nanoparticles prepared *via* chemical and electrochemical routes is reviewed. The preparation of palladium nanoparticles with well-controlled particle sizes and shapes (17, 18) of a high monodispersity is a key technology in producing materials that are more effective and efficient than the current state of the art. For example, particle size can play a critical role in a catalytic process and a monodispersed particle with an optimal size enables the most efficient use of the valuable metal and the highest selectivity in the subsequent reaction.

2. Types of Stabilisation

As nanoparticles are essentially finely divided bulk materials, they are typically thermodynamically unstable with respect to agglomeration. Consequently, they need to be kinetically stabilised and this is typically done using a protective stabiliser. The stabilisation is achieved by electrostatic or steric forces or a combination of the two (electrosteric forces). The stabiliser is typically introduced during the formation of the nanoparticles, and this is achieved *via* the chemical or electrochemical reduction or thermal decomposition of metallic precursors. The subsequent interaction between the stabiliser and the surface of the nanoparticle is a highly dynamic one, with its strength and nature often controlling the long-term stability of a dispersion of the nanoparticles. This interaction can take many forms, such as a strong covalent linkage (as in the case of a thiol), a chemisorbed atom (for example *via* a lone pair of a heteroatom in a polymer) or an electrostatic interaction with a layer of anions (within a double layer structure of a surfactant).

The formation of palladium nanoparticles stabilised by the most common stabilisers (organic ligands, surfactants, polymers and dendrimers) (**Figure 1**) are discussed below.

3. Ligands

One of the most frequent methods of stabilising palladium nanoparticles is by the addition of an organic ligand that typically contains a heteroelement bearing an accessible lone pair. The organic chain of the ligand prevents agglomeration, whilst the heteroatom binds strongly to the surface of the metal.

3.1 Sulfur-Based Ligands

The strong interaction between the platinum group metals and soft sulfur-based donors make sulfur-containing ligands highly efficient stabilisers for nanoparticles. In the 1990s, Brust demonstrated that thiols made excellent stabilisers in the two-phase preparation of gold nanoparticles (19). The 1–3 nm diameter nanoparticles were stabilised by a monolayer of thiolate ligands and were readily isolable as dry powders and, subsequently, redispersable into non-polar solvents. This methodology has been used to prepare nanoparticles containing a wide range of precious metals including palladium. In general, it is the use of thiol and thioether ligands that

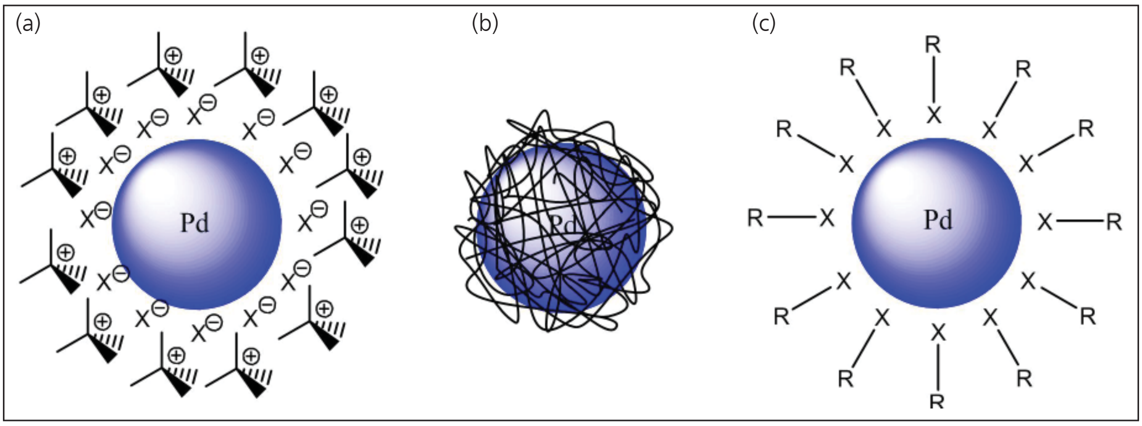


Fig. 1. Schematic representing the stabilisation of palladium nanoparticles using different protecting groups: (a) surfactants; (b) polymers; and (c) ligands

dominates the literature due to the high stability of the nanostructures that they can generate.

The use of sulfur-based ligands to stabilise palladium nanoparticles usually restricts their use as potential catalysts due to the poisoning effect of sulfur (20). However, this effect is not universal. For example, dodecylthiolate-stabilised palladium nanoparticles have been shown to be active catalysts for the formation of carbon nanotubes (21). Furthermore, they have been demonstrated to be a stable and recyclable catalyst in the Suzuki-Miyaura C–C coupling reaction of halogenoarenes and phenylboronic acid (**Figure 2**) (22), while thiolated β-cyclodextrin (HS-β-CD)-stabilised palladium nanoparticles have shown good activity in the hydrogenation of allylamine (**Figure 2**) (23).

3.1.1 Thiol Ligands

Alkanethiol-protected palladium nanoparticles can be directly prepared *via* the two-phase Brust methodology (**Figure 3**) (24). Typically, a tetrachloropalladate salt is initially phase transferred from aqueous to organic solution (in solvents such as dichloromethane or toluene) by the addition of a long-chain ammonium salt (for example, tetra-*n*-octylammonium bromide or Aliquat 336®). The stabilising ligand is then added to the organic phase prior to reduction with an aqueous solution of sodium borohydride. The ligand is usually introduced as a long-chain thiol molecule; however, the *in situ* reduction of an alkylsulfate (such as *S*-dodecylthiosulfate (25)) has been demonstrated to be an effective alternative strategy.

The size and morphology of the resulting palladium nanoparticles are sensitive to a number of different reaction conditions (26). These include the surfactant used (27), the reducing agent employed, the reaction time, the nature of the stabilising ligand (28), and the ratio of the palladium precursor to the other reagents (29). In general, to prepare small nanoparticles it is beneficial to use a large excess of long thiols with an excess of reducing agent (26).

The Brust route has proved to be an excellent preparative technique for the formation of nanoparticles stabilised by simple lipophilic

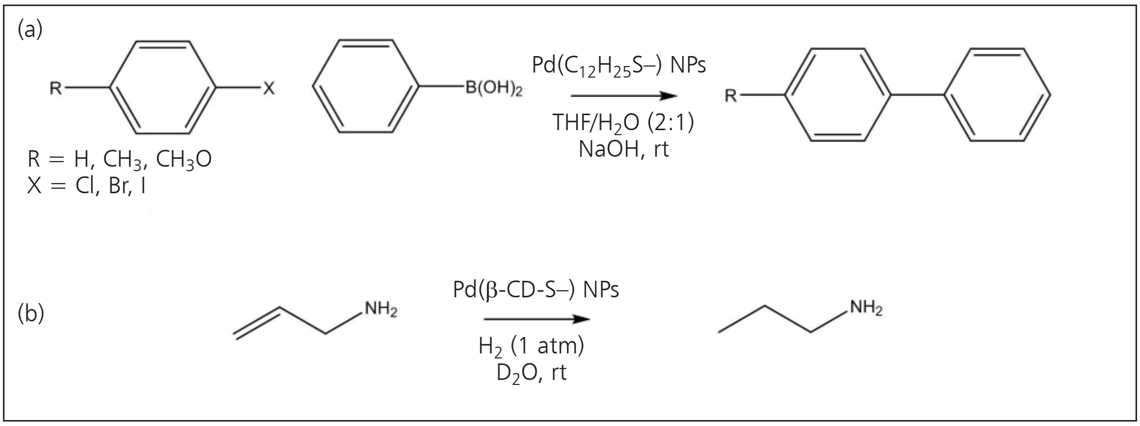


Fig. 2. Reported catalytic transformations using thiol-stabilised palladium nanoparticles (NPs): (a) Suzuki-Miyaura carbon–carbon coupling reaction of halogenoarenes and phenylboronic acid (22); and (b) hydrogenation of allylamine (23)

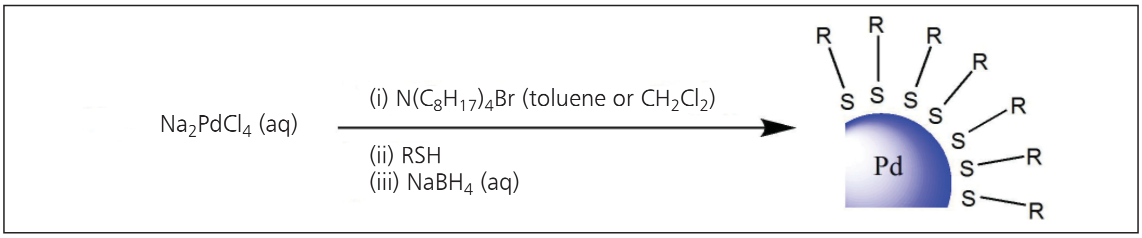


Fig. 3. Scheme illustrating the synthesis of thiol-stabilised palladium nanoparticles using the modified Brust method (24)

n-alkanethiols (24). The use of a two-phase system also allows the organically soluble nanoparticles to be simply separated from the aqueous byproducts. However, when more polar ligands are used, the purification is less facile. There have been several variations that have enabled the fabrication of complementary nanoparticles that are soluble in aqueous or polar solvent systems.

An alternative synthetic approach allowing a wider variety of ligands to be used was achieved by Ulman and coworkers, who employed Super-Hydride® (lithium triethylborohydride, $LiEt_3BH$) as a reductant (30). The combination of palladium(II) acetate with octylthiol resulted in a soluble metal-thiolate complex in tetrahydrofuran (THF). Addition of Super-Hydride® solution to this resulted in stable nanoparticles being formed with an average diameter of 2.3 nm.

Whilst the Super-Hydride® route allows stabilisers (such as hydroxyl-terminated alkylthiols) to be used that cannot be used in the two-phase reaction, and also avoids the use of phase transfer surfactants, there are limited solvent systems that can be used and the reductant is less easy to handle than sodium borohydride.

An alternative strategy for preparing palladium nanoparticles that are soluble in aqueous systems has been the use of ω-substituted thiol ligands (those terminated with a charged functional group, such as ammonium or carboxylate salts). Indeed, the one-phase sodium borohydride reduction of potassium tetrachloropalladate(II) in the presence of the chloride salt of the *N,N*-trimethyl(undecylmercapto)ammonium ligand yielded water-soluble palladium nanoparticles with an average diameter of 2.7 nm (± 1.1 nm) (31).

Similarly, the functionalisation of water-soluble hosts with thiol groups enables the preparation of ligands that can stabilise the formation of palladium nanoparticles in aqueous solvent systems. Cyclodextrins are highly functionalised water-soluble hosts that can easily be synthetically modified (32). The sodium borohydride reduction of a dimethyl sulfoxide-water solution of the per-6-thio-β-cyclodextrin and sodium tetrachloropalladate(II) produces a colloidal dispersion (**Figure 4**) (23). The nanoparticles were shown to be active in hydrogenation reactions and could also be easily recovered by precipitation with ethanol.

For many precious metal nanoparticles, a successful way to introduce functionality to preformed nanoparticles is *via* ligand exchange (33, 34). Typically, the addition of a second ligand can statistically displace those bound to the surface of the particle without destroying the size of the metallic core. For example, the addition of a thiol ligand containing electrochemically active ferrocene derivatives could displace hexanethiol- and dodecanethiol-stabilising molecules (35), thus providing additional functionality to the nanomaterial. In addition, the replacement of one ligand by another may be desirable in order to alter the solubility of the nanoparticles (for example, from organic to aqueous solvent systems (36)) or

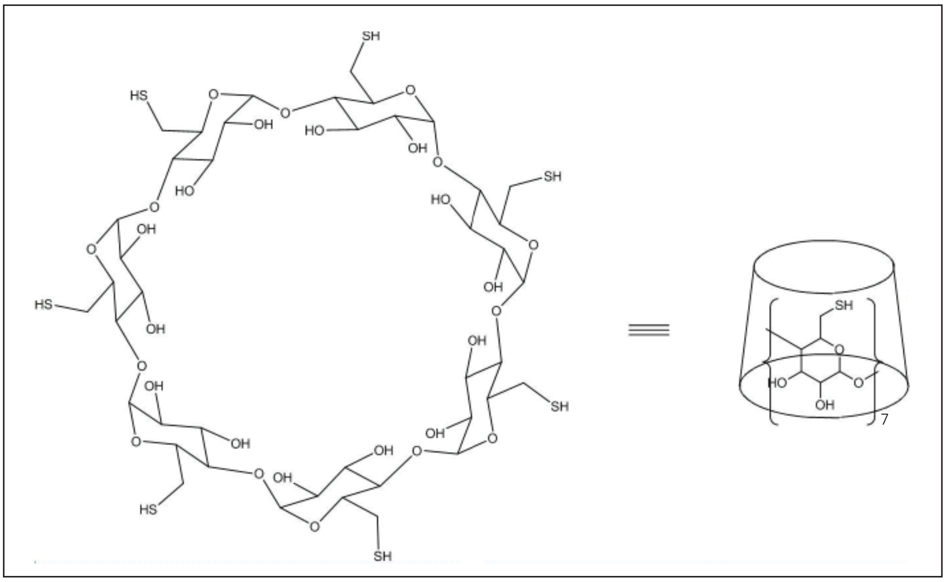


Fig. 4. Structure of thiol functionalised beta-cyclodextrin per-6-thio-β-cyclodextrin (HS-β-CD) (23)

to improve their solubility by introducing a better stabilising group (26, 37).

3.1.2 Other Sulfur-Based Ligands

Given that there is much literature on the stabilisation of palladium nanoparticles by thiol ligands and that there is a strong interaction between palladium and sulfur, there are surprisingly few other sulfur-based ligands that have been reported as stabilisers. Two such examples are the thioether (38) and thioester (39) functional groups. The interaction between these groups and the metal surface is weaker than for thiols as the ligand is unable to form anionic species *via* the same mechanism by which thiols readily form thiolates. However, this can lead to advantages, with greater surface accessibility in applications such as catalysis and facile post-synthetic modifications *via* ligand displacement reactions (40).

The use of thioethers has enabled stabilised palladium nanoparticles to be prepared on a gram scale by heating palladium(II) acetate in the presence of an excess of the ligand (38). It was found that thioether chains greater than six carbons in length were required to form stable dispersions with a narrow particle size distribution, with longer chain lengths giving rise to smaller particle sizes. Furthermore, *n*-dodecylsulfide stabilised palladium nanoparticles were shown to be active hydrogenation catalysts for a range of olefins when used either unsupported or following deposition onto silica. This illustrates the accessibility of the surface when such ligands are employed and their potential benefits in catalytic applications.

3.2 Phosphorus-Based Ligands

The use of phosphorus-containing compounds in the formation of nanosystems dates back to the 19th century, when Faraday prepared gold nanoparticles by reducing tetrachloroaurate salts with phosphorus vapours (41). It is therefore not surprising that they have subsequently been exploited in the stabilisation of precious metal nanoparticles and subsequent catalytic transformations (42, 43).

The use of phosphine ligands has been reported by several authors for the preparation of monodisperse palladium nanoparticles. Hyeon and coworkers reported how the thermolysis of a preformed palladium-trioctlyphosphine (TOP) complex yielded such nanoparticles (44). The mean size could be varied depending on the reaction conditions. For example, 3.5 nm nanoparticles were formed when $Pd(acac)_2$ (acac = acetylacetonate) and TOP were heated to 300ºC under an argon atmosphere. When TOP was used in combination with oleylamine as a stabiliser and solvent, larger monodispersed nanoparticles up to 7.5 nm could be formed.

A further benefit of phosphine ligands is the presence of a nuclear magnetic resonance (NMR) active nucleus in close proximity to the metal surface. Examination of ^{31}P NMR spectra has given insights into the coordination of phosphorus-based ligands to metal surfaces (45). The coordination of the phosphine ligand to a palladium nanoparticle typically results in a downfield shift in the ^{31}P NMR peaks compared to that of the free ligand, such that it resembles that of a Pd(0)-phosphine coordination complex. While this is the case for triphenylphosphine-stabilised palladium nanoparticles, the bond to the surface is weaker in TOP and, consequently, the shift is not as great. It is thought that strong van der Waals interactions between the alkyl chains in the different TOP ligands hinder the effective adsorption of TOP ligands onto the surface of the palladium nanoparticles.

In addition to the direct preparation of phosphine-stabilised nanoparticles, indirect ligand exchange reactions can also be successfully undertaken. These reactions are particularly effective when TOP-stabilised palladium nanoparticles are used, as the weak binding of the ligand on the surface allows easy displacement. Son *et al.* demonstrated that a wide variety of mono- and bi-dentate phosphines could be used to exchange with TOP (**Figure 5**) (45). The methodology was also used to introduce hydrophilic phosphines, which were able to solubilise the resulting nanoparticles in aqueous solvent systems. All of the exchange reactions were achieved while maintaining the monodispersity and particle size of the initial nanoparticles.

The preparation of phosphine-stabilised palladium nanoparticles has also been undertaken by Fujihara and coworkers using a two-phase process. They adapted an existing route for preparing analogous gold nanoparticles (46) by phase transferring potassium tetrachloropalladate(II) into dichloromethane using tetraoctylammonium bromide before sodium borohydride reduction in the presence of optically active bidentate BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) ligands (**Figure 6**) (47).

The use of chiral (*R*)- and (*S*)-BINAP gave rise to the corresponding chiral palladium nanoparticles, for which circular dichroism spectra showed positive and negative Cotton effects, respectively. The nanoparticles were also effective as a catalyst in the hydrosilylation

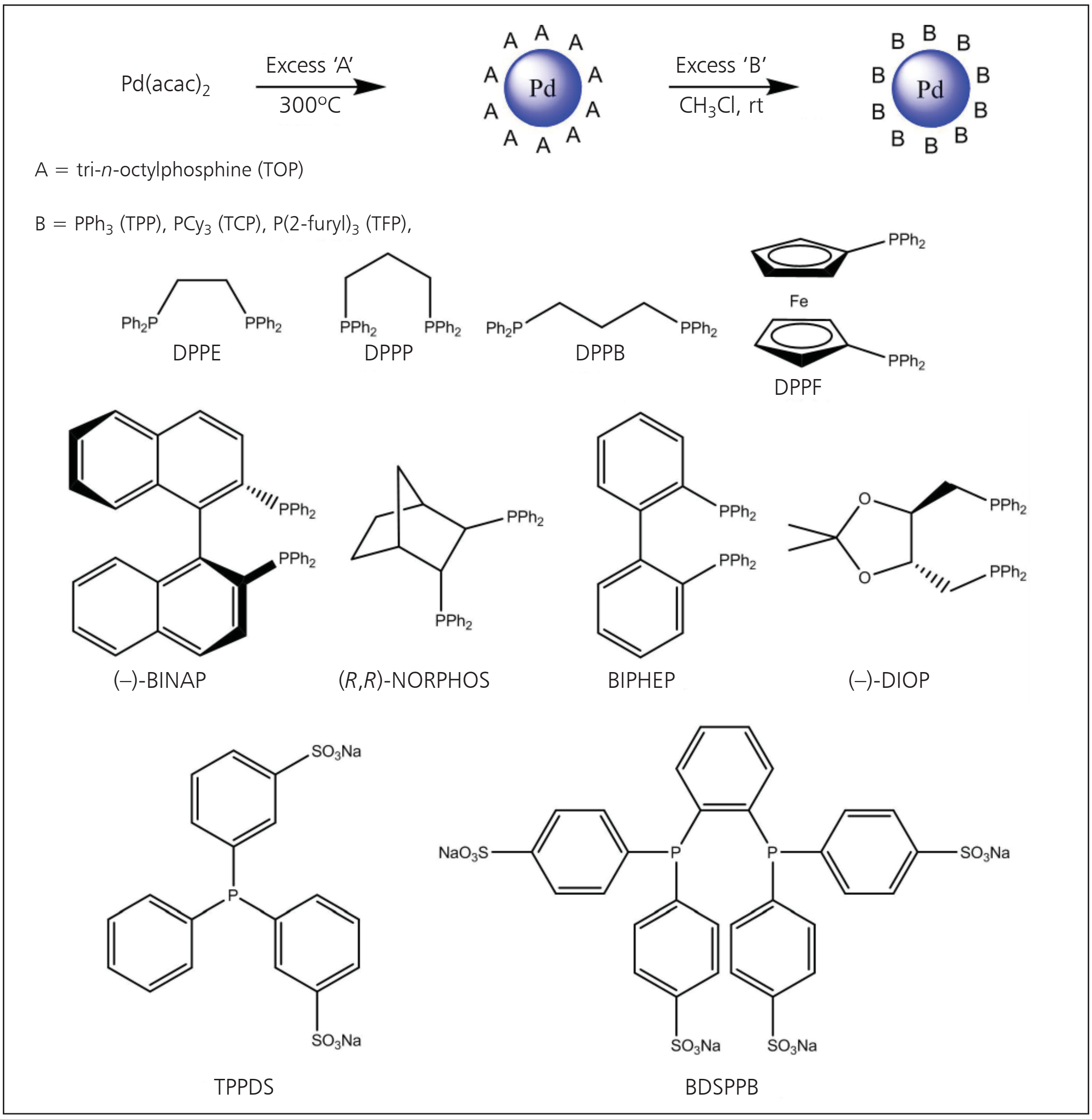


Fig. 5. Formation of phosphine-stabilised palladium nanoparticles via direct thermolysis and subsequent ligand exchange reactions (45)

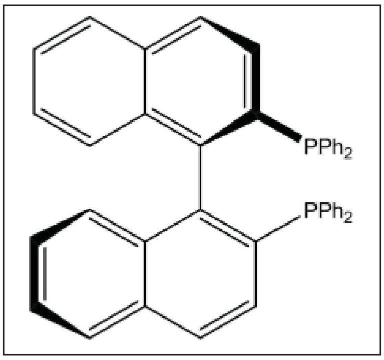


Fig. 6. Structure of the optically active (R)-BINAP ligand (47)

of styrene with trichlorosilane, leading to the formation of an asymmetric product. Subsequent oxidation using hydrogen peroxide retained the chiral centre and yielded optically active 1-phenylethanol in an enantiomeric excess of 75%. This revealed the active role of the chiral ligand surrounding the palladium nanoparticles as both a promoter and an asymmetric induction reagent.

Palladium nanoparticles stabilised by BINAP-thioether-derivatives have also been used in the (quasi) homogeneous C–C coupling reactions (**Figure 7**) (48). The presence of the chelating diphosphine ligand provided remarkable stability to the nanoparticles, preventing their aggregation throughout the process. Furthermore, the nanoparticles could be subsequently isolated and reused without any loss of catalytic activity.

3.3 Nitrogen-Based Ligands

The use of electron-rich nitrogen-containing ligands has been extensively used to stabilise precious metal nanoparticles. The lone pair of the nitrogen species (such as long-chain primary amines) is able to strongly chemically adsorb onto the surface of the metal, with the alkyl group preventing agglomeration *via* steric stabilisation.

Mazumder and Sun prepared monodispersed palladium nanoparticles by reducing $Pd(acac)_2$ in oleylamine with boron tributylamine (BTB) at 90ºC (**Figure 8**) (49). The oleylamine served as a solvent, stabilising ligand and reductant, with BTB as a coreductant. When oleylamine alone was used as a stabiliser/solvent, higher reaction temperatures were required and, subsequently, transmission electron microscopy (TEM) showed that larger and more polydispersed nanoparticles were formed (44).

A wide range of alternate primary amines can also be employed in this one-phase reaction. However, using the saturated analogue dodecylamine did not provide such high quality nanoparticles, suggesting that the double bond present in oleylamine plays a crucial role in particle stabilisation and the control of the growth process. Furthermore, the palladium precursor used was also observed to have a significant effect on the nanoparticles formed. The acac salt gave more monodispersed distributions than the corresponding nitrate or chloride salts. It is possible that the carbon monoxide molecules generated *in situ* from the decomposition of the acac ligand also play a key role in controlling the particle growth process (44).

Primary amines have also been employed in two-phase reactions. Choi and coworkers demonstrated that particle size could be altered by varying the initial ratio of palladium(II) chloride to amine and the length of the alkyl chain (50). The particle size decreased

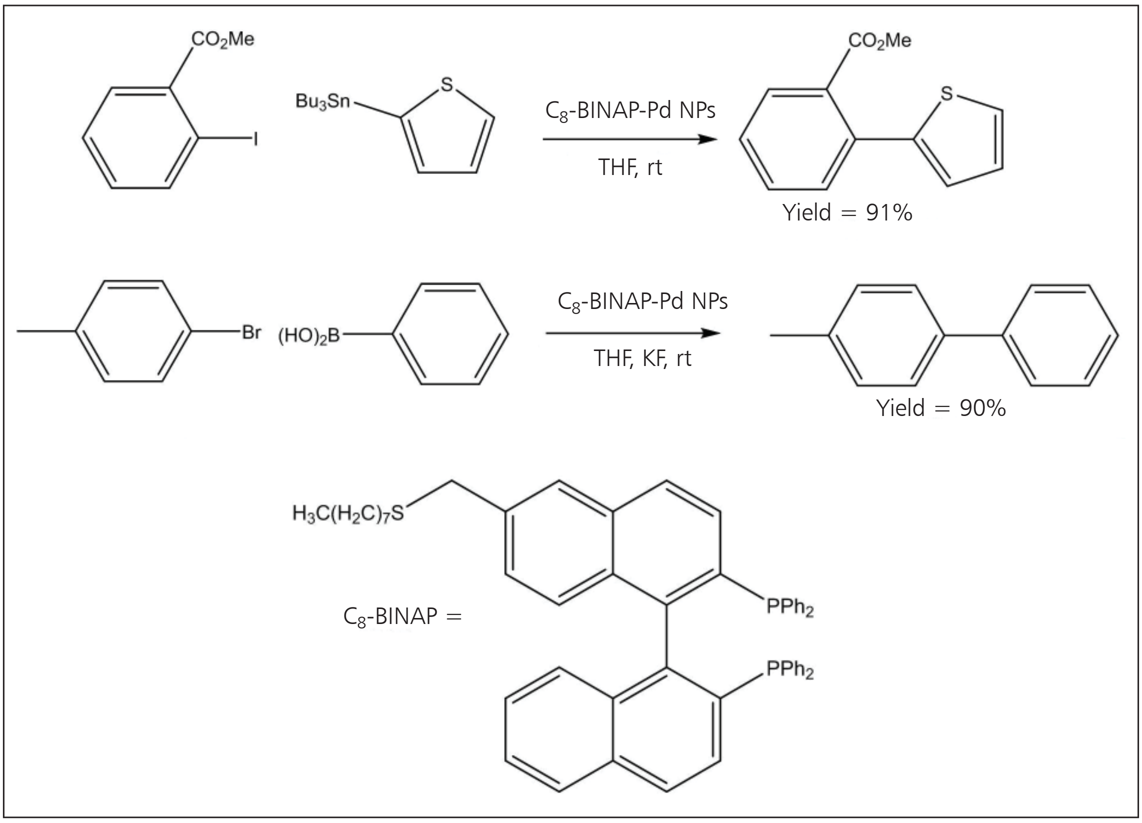


Fig. 7. (Quasi)-homogeneous carbon–carbon coupling reactions undertaken by BINAP thioether-derivatised palladium nanoparticles (48)

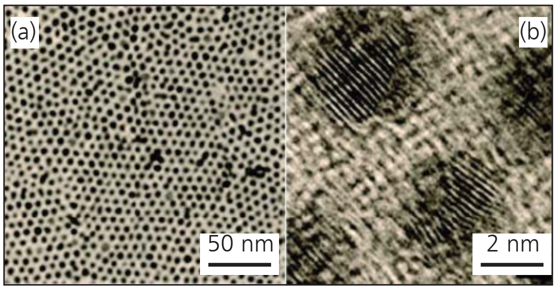


Fig. 8. (a) TEM; and (b) high resolution-TEM images of 4.5 nm Pd nanoparticles prepared by the reduction of Pd(acac)$_2$ in oleylamine and BTB (Reprinted with permission from (49). Copyright 2009 American Chemical Society)

with increasing chain length, which corresponded to superior catalytic performance in the electrochemical oxidation of methane.

This demonstrates that, despite the presence of amine groups, palladium is still able to act effectively as a catalyst, largely due to the resulting accessibility of the metal surface. The surface accessibility has been examined by ^{1}H NMR studies, which show that fast exchange occurs between free and uncoordinated amine ligands at the surface of the palladium nanoparticles (51). In contrast, polyphosphine ligands do not display fast exchange, with the ligands firmly coordinated on the surface of the nanoparticles. The weaker binding of the amino ligands makes them more attractive for use in catalytic processes. Furthermore, the presence of the ligand on the surface may even provide additional protection to the palladium nanoparticle when corrosive solvent systems are employed.

In addition to aliphatic amines, several other nitrogen-containing molecules have been used to stabilise palladium nanoparticles. These include aromatic amines (52), porphyrins (53), pyridyl groups (54) and imidazole derivatives (55).

The readily available 4-dimethylaminopyridine (DMAP) ligand has been widely explored as a stabiliser for metal nanoparticles. Of these, palladium-based systems have been used as catalytic microcapsules, exploiting the non-bulky nature of the ligand, thereby allowing access to the particle surface by organic reactants (56).

Although the synthesis of DMAP-stabilised palladium nanoparticles has been undertaken *via* the reduction of sodium tetrachloropalladate(II) using sodium borohydride in aqueous conditions (57), its use has been better documented in a ligand exchange reaction (54). Gittins and Caruso prepared tetraalkylammonium bromide-stabilised palladium nanoparticles in a two-phase (toluene/water) reaction (**Figure 9**) (54). Addition of an aqueous solution of DMAP gave rise to rapid and complete transfer of the nanoparticles into the aqueous phase. This not only offers a simple and effective method of transferring nanoparticles into aqueous media, but also allows the particle size of the initial palladium nanoparticle to be maintained.

Recently, Serpell *et al.* have demonstrated that imidazole derivatives can also be used as effective stabilisers for palladium nanoparticles and the subsequent deposition of these onto activated carbon gives rise to an active catalyst for hydrogenation reactions (55). Furthermore, the addition of hydrogen bond donors into the aliphatic chain of the imidazole derivative has proved efficient in preparing core-shell nanoparticle structures. For example, an appended amide group is able to bind an anionic metallic salt in close proximity to the surface of the nanoparticle and its subsequent reduction generates the desired core-shell structure (**Figure 10**). When gold is added to a preformed palladium nanoparticle in this way, the selectivity of the resulting catalyst in the catalytic hydrogenation of 2-chloronitrobenzene to 2-chloroaniline is dramatically enhanced by the core-shell system.

3.4 Other Ligands

In general, ligands containing heteroatoms stabilise precious metal nanoparticles by forming strong bonds with the surface. However, recently there have been examples of nanoparticles being stabilised with carbon-based ligands (58, 59). Palladium has been extensively used as the contact metal of choice in the fabrication of carbon nanotube-based nanoelectronic devices and circuitries because of its low contact resistance (60, 61), and so it is not unexpected that carbon can be used to stabilise nanoparticles. In fact, the bonding energy for a Pd–C single bond is 436 kJ mol^{-1}, even larger than that of the Pd–S linkage (380 kJ mol^{-1}) (62).

Stable palladium nanoparticles have been prepared by passivating the metal cores with Pd–C covalent linkages by using diazonium derivatives as precursors (62). The addition of Super-Hydride® to palladium(II) chloride resulted in the generation of nanoparticles. Simultaneously, aliphatic radicals generated by the reduction of diazonium ligands formed the strong Pd–C linkages. A range of

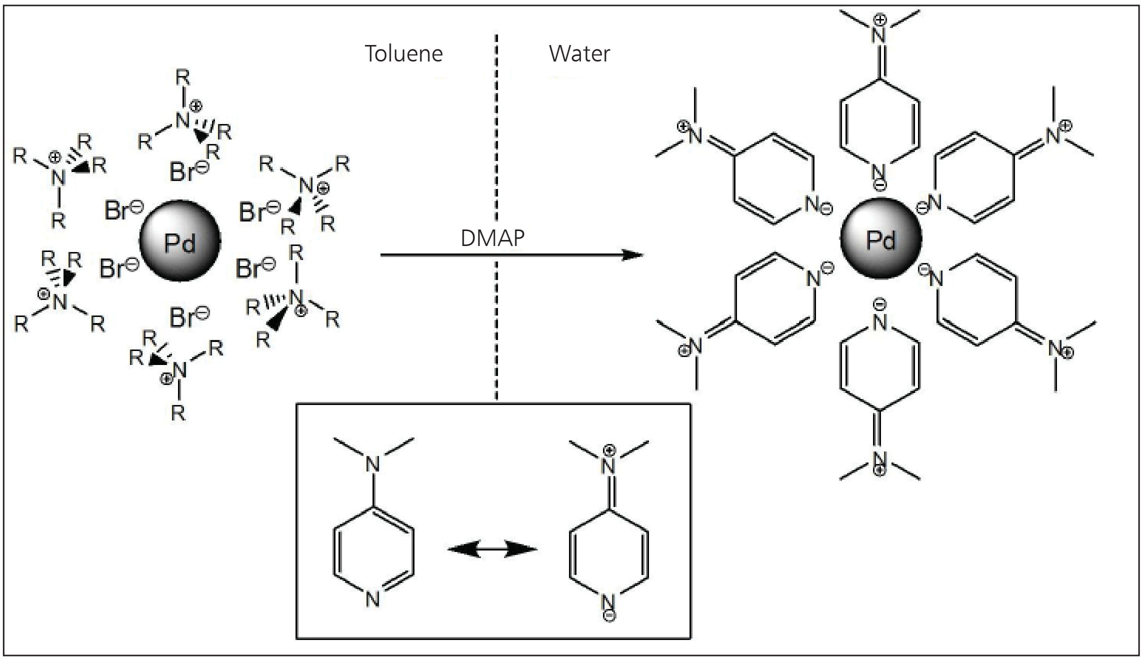


Fig. 9. Partitioning of palladium nanoparticles from organic to aqueous solvent systems via the addition of DMAP to tetraalkylammonium bromide-stabilised nanoparticles. Inset shows the resonance structures of DMAP illustrating the high electron density present on the donor nitrogen

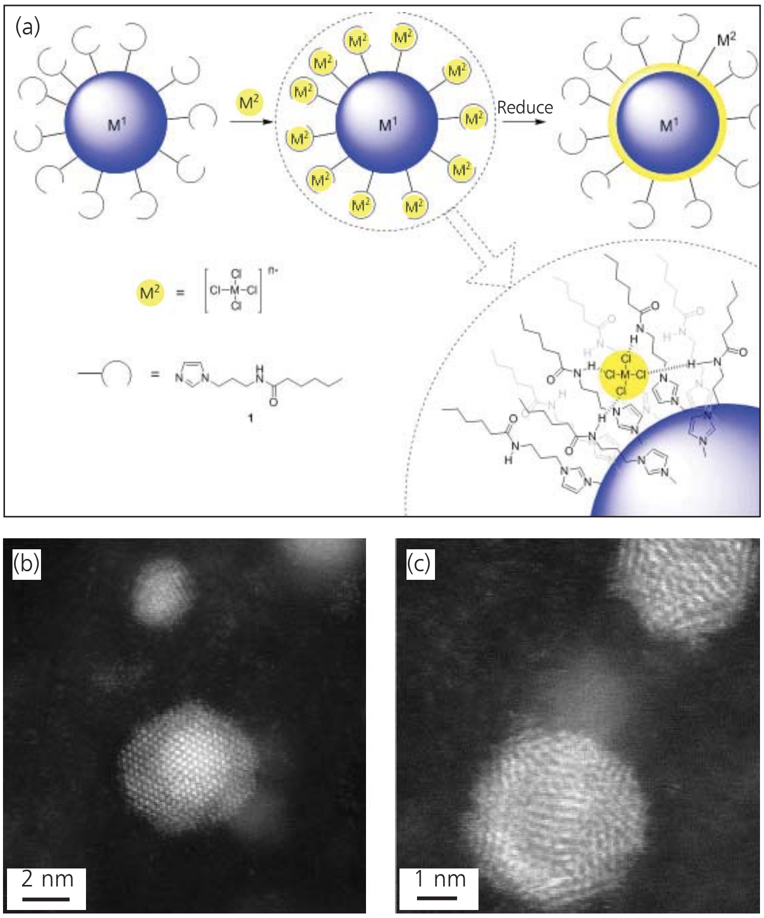


Fig. 10. (a) Preparation of imidazole-stabilised palladium-based nanoparticles. The use of an anion binding group on the backbone of the ligand enables well-defined core-shell nanoparticles to be prepared. Aberration-corrected high angle annular dark field STEM images clearly show the formation of the (core@shell) materials; (b) Au@Pd; and (c) Pd@Au nanoparticles (55)

spectroscopic and microscopic measurements were consistent with the formation of carbon-stabilised palladium nanoparticles (**Figure 11**).

4. Surfactants

The use of salts/surfactants is a popular route to stabilising metal nanoparticles. Frequently, tetra-*N*-alkylammonium halide salts are chosen for this purpose, although other analogous materials (such as imidazolium-based ionic liquids (63–65)) can act as stabilisers using the same mechanism. Here the stabiliser is able to prevent irreversible agglomeration of the metal *via* a combination of electrostatic and steric effects (66). It is thought that surfactant-stabilised nanoparticles strongly adsorb a layer of anions to the surface of the metal, which in turn are surrounded by a layer of countercations, in order to retain electroneutrality (**Figure 12**) (4, 67, 68). Both elements of the surfactant play a key role in protecting the metal from agglomeration. Varying the nature of the cationic component allows the nanoparticles to be dispersed in either organic or aqueous media. Furthermore, surfactants such as cetyltrimethylammonium bromide (CTAB) enable the generation of anisotropic particle shapes (69).

Bönneman demonstrated that the choice of metal salt used was also vitally important (70). For example, the hydrogen reduction of $[(\text{octyl})_4\text{N})]_2\text{PdCl}_4$ only gave a metallic precipitate, whereas the reduction of $[(\text{octyl})_4\text{N})]_2\text{PdBr}_4$ by hydrogen does not occur, even at 50 bar H_2. In contrast, the hydrogen reduction of $[(\text{octyl})_4\text{N})]_2\text{PdCl}_2\text{Br}_2$ in THF yields 4 nm nanoparticles, albeit after fourteen days.

Many routes have been employed for the synthesis of surfactant-stabilised palladium nanoparticles. Gittins and Caruso prepared tetra-*n*-octylammonium bromide (TOAB) stabilised palladium nanoparticles in a two-phase (toluene/water) reaction (54). This is a modification of the Brust route, which used thiol ligands. In the modified method, the ammonium salt acts as both a quantitative phase transfer agent and a stabiliser. Subsequent work has illustrated that the two key parameters to obtain small nanoparticles with a narrow size distribution

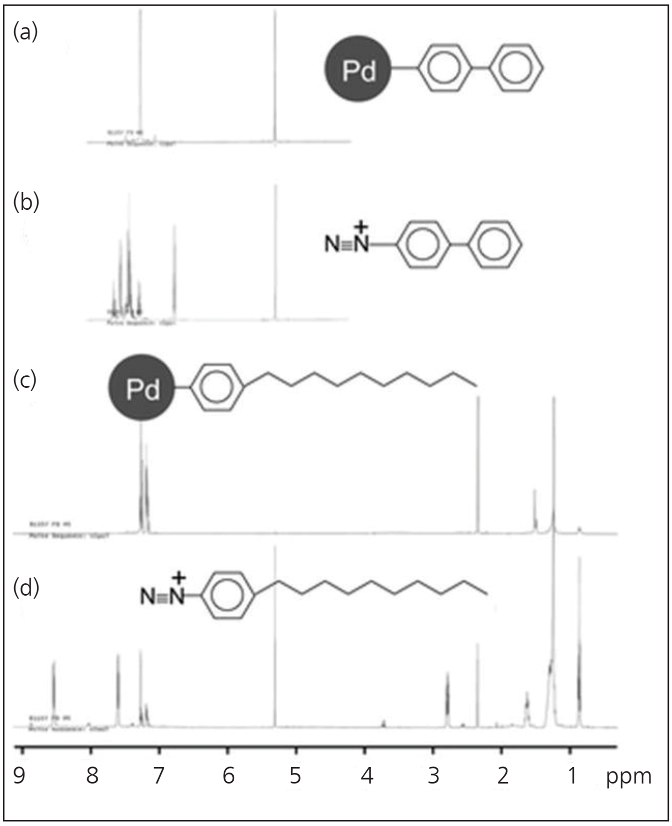


Fig. 11. ^{1}H NMR spectra of Pd nanoparticles stabilised by metal-carbon bonds: (a) Pd–BP; (b) biphenyldiazonium (BP); (c) Pd–DP; and the parental diazonium ligands; and (d) decylphenyldiazonium (DP). The samples were all prepared in $CDCl_3$ (62) (Copyright © 2008, Royal Society of Chemistry. Reproduced with permission)

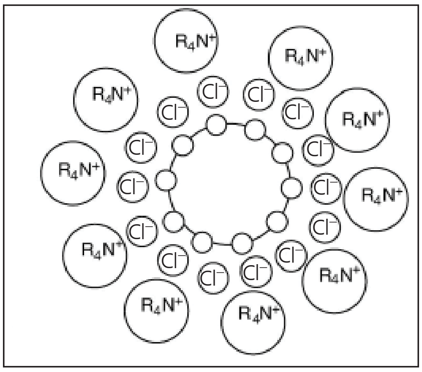


Fig. 12. 'Electrosteric' stabilisation of a nanoparticle by a surfactant. Halide ions are in close proximity to the positively charged nanoparticle surface and surrounded by the sterically bulky tetrabutylammonium countercations (Reprinted with permission from (4). Copyright 2007 American Chemical Society)

were the concentration of the capping agent and the stirring rate used upon addition of the reductant (71). The latter can be explained by considering that the reduction of Pd(II) to Pd(0) occurs at the phase boundary (organic to aqueous). Therefore, controlling the size of the water droplets formed in the toluene/water mixture has a dramatic effect on the subsequent particle size.

A similar approach was adopted by Bönneman and coworkers (72), who combined the stabilising agent (NR_4^+) with the reducing agent to allow a high local concentration of the stabiliser to build up at the reduction centre (entropic stabilisation factor), which reduces the need to add an excess of the capping agent or reductant. However, this has the disadvantage that a stoichiometric ratio of the two is always maintained and an additional cost of preparing the reducing agent is present (**Figure 13**) (72).

Reetz also employed surfactants as stabilisers for palladium nanoparticles, but using an electrochemical synthetic procedure (**Figure 14**) (3). By using an electrochemical cell with a sacrificial palladium anode as the metal source, and with the supporting electrolyte also acting as a source of stabilising surfactant, stable nanoparticles can be formed (73). Varying the current density influences the particle size, with higher current densities giving rise to smaller nanoparticles. The synthesised nanoparticles precipitate out of the initial acetonitrile/THF solvent system, but are subsequently redispersible. Altering the surfactant can dramatically alter the solubility of the nanoparticles – for example, using tetraoctadecylammonium bromide gives nanoparticles that are soluble in organic solvents; whereas using sulfobetaine 3-(*N*,*N*-dimethyldodecylammonio)propanesulfonate gives nanoparticles that are soluble in aqueous solvent systems.

One of the major advantages of using surfactants as protecting agents for nanoparticles is that their relatively weak and poorly defined interactions with the metal surface give reagents a high degree of accessibility to the surface of the nanoparticles. This feature has been exploited in ligand exchange reactions (where the surfactant can be displaced by a stronger binding ligand (54)) as well as in catalysis. For example, tetra-*n*-alkylammonium halide-stabilised palladium nanoparticles have demonstrated good catalytic activity in liquid phase hydrogenation reactions. However, as alluded to earlier, over time the nanoparticles precipitate out of solution under a hydrogen atmosphere and are therefore ineffective as semi-homogeneous catalysts. However, once immobilised onto a solid support, the nanoparticles remain active and the heterogeneous catalyst can undergo numerous turnovers (74).

5. Steric Stabilisation (Polymers and Dendrimers)

The stabilisation of nanosystems can also be achieved by incorporating them within an organic matrix, which can be either a flexible polymer or a more preorganised dendritic structure. The steric bulk of this class of stabilising agents prevents agglomeration of the nanoparticles to bulk metal (75, 76).

$$MX_n + nNR_4(BEt_3H) \xrightarrow{\qquad\qquad} M_{NP} + nNR_4X + nBEt_3 + n/2H_2$$

M = metals of Groups 6–11; X = Cl, Br; n = 1, 2, 3; R = alkyl, C_6–C_{20}

Fig. 13. Bönneman's method of preparing metal nanoparticles by combining the reductant and the stabilising surfactant (72)

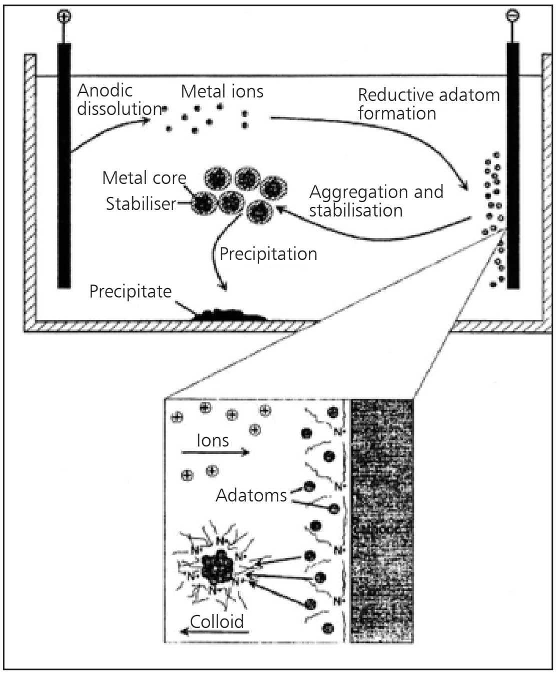


Fig. 14. Reetz et al.'s postulated mechanism for the formation of electrochemically synthesised surfactant ($R_4N^+X^-$)-stabilised nanoclusters (3) (Copyright © 1999, Elsevier. Reproduced with permission)

5.1 Polymers

Polymers, such as poly(*N*-vinyl-2-pyrrolidone) (PVP) and poly(vinyl alcohol) (PVA), are widely used to protect nanoparticles because of their commercial availability at relatively low cost and their solubility in a range of solvents, including water (**Figure 15**) (77, 78). The use of polymers is often associated with the 'polyol method', in which a metal precursor is dissolved and reduced at high temperatures by an alcohol (typically ethylene glycol) (78, 79). The standard procedure requires several hours of reflux to fully reduce the precursors to their metallic state, although the process can be hasted by irradiating the sample with microwaves (80, 81). The use of alcohols as reducing agents offers the advantage that any byproducts are simple organic compounds, unlike the residues of other reducing agents, such as borane derivatives (82).

In particular, PVP, poly(*N*,*N*-dialkylcarbodiimide) and polyurea-stabilised palladium nanoparticles give highly efficient catalysts for Suzuki-Miyamura reactions (83, 84). In addition, palladium-catalysed Suzuki and Stille cross-couplings of aryl bromides and chlorides were carried out under mild conditions and with the recycling of the catalyst (84).

5.2 Dendrimers

Dendrimers are macromolecules that, unlike polymers, are perfectly defined on the molecular level (85, 86). Their internal cavities behave as molecular boxes that can entrap and stabilise metal nanoparticles, especially if there are heteroatoms present in the interior of the dendrimer. Two families of dendrimer have been extensively studied and are commercially available: poly(amidoamine) (PAMAM) and poly(propylene imine) (PPI) (**Figure 16**). Both of these have been employed in the synthesis of numerous metallic nanoparticles (87, 88).

In order to prepare palladium-encapsulated nanoparticles, metal ions are generally sorbed into the interior of the dendrimer. Subsequent reduction yields nanoparticles that remain encapsulated within the structure of the macromolecule, which prevents agglomeration to bulk metal (89). The size of the nanoparticles is primarily determined by the number of palladium(II) species preloaded into the dendritic structure and the generation of the dendrimer limits the particle size and maximum metal loading that is possible. Typically, nearly monodispersed nanoparticles in the range of 1–3 nm with a high proportion of accessible metal sites are prepared by this route (90). Whilst the interior of the dendrimer can be tuned to control the metal nanoparticles, the periphery of the dendrimer can also be modified to allow solubility in either organic (91), aqueous (92), supercritical carbon dioxide (93), or fluorous media (87).

There has been considerable research into using dendrimer-stabilised nanoparticles for applications such as catalysis (94, 95). The cavities of the dendrimer are sufficiently porous to allow the passage of substrates and products to and from the reaction media and the surface of the metal. Furthermore, adjusting the 'mesh' of the dendrimer allows control over the rate of reaction and the selectivity of the catalytic process (**Figure 17**) (94, 96).

Dendrimer-encapsulated nanoparticles can also be used in quasi-homogeneous reactions, with the advantage that the process can be controlled due to the well-defined dendritic structure. For instance, the catalytic activity toward the hydrogenation of allyl alcohol and *N*-isopropylacrylamide by hydroxyl-terminated PAMAM dendrimer containing palladium nanoparticles has been shown to be strongly affected by the structure of the stabiliser. In particular, catalysts based on high-generation dendrimers have been found to be selective towards linear substrates, because of their low porosity (96, 97).

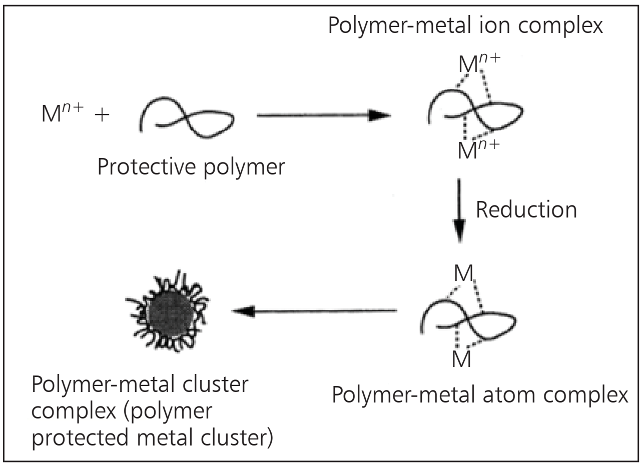
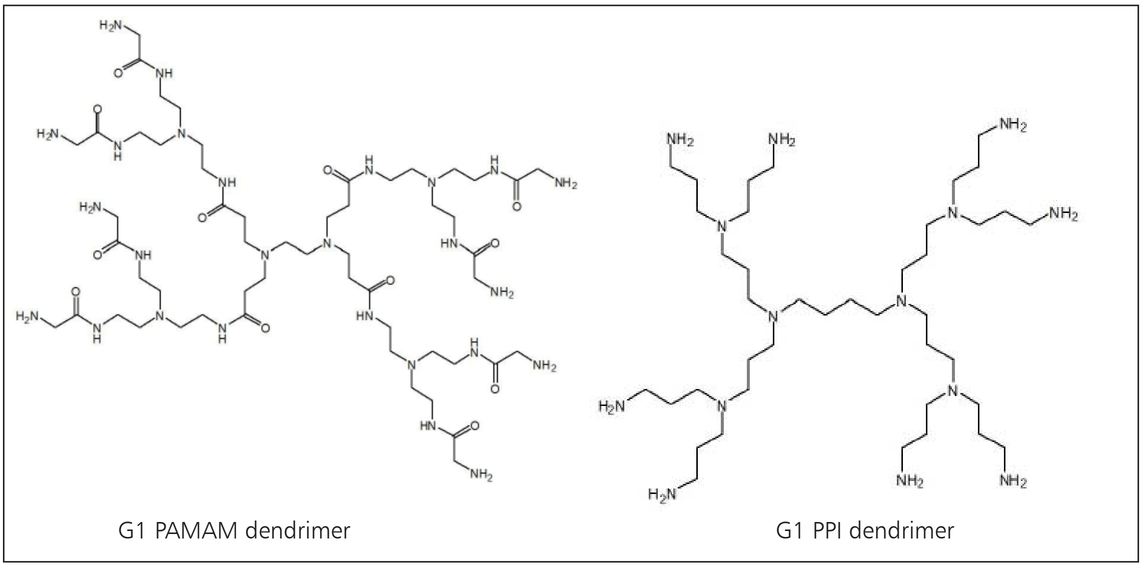


Fig. 15. Schematic representation of the reduction process of metal salts in the presence of a stabilising polymer (78) (Copyright © 1998, Royal Society of Chemistry. Reproduced with permission)


G1 PAMAM dendrimer

G1 PPI dendrimer

Fig. 16. Structures of the two most commonly used dendrimer building blocks: poly(amidoamine) (PAMAM) and poly(propylene imine) (PPI)

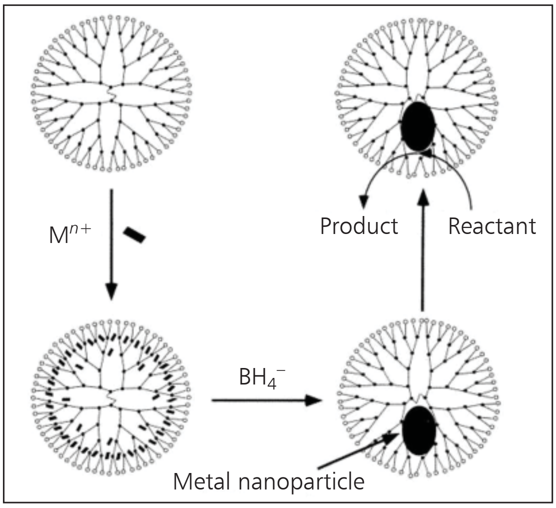


Fig. 17. Representation of the formation of metallic nanoparticles within a dendritic structure and their subsequent application in catalysis (Reprinted with permission from (94). Copyright 2001 American Chemical Society)

5.3 Other Bulky Ligands

Recently, the use of sterically bulky biomolecules (such as proteins, polypeptides and DNA) has attracted attention for controlling the growth of water-soluble metal nanoparticles (98–101). Furthermore, the functionalised nanoparticles offer a range of bio-related applications, including the assembly of hybrid structures, and biodetection (102). Varying the amino acid sequence in stabilising peptide chains has been shown to have a significant effect on particle size, as a peptide can act not only as a stabiliser but also as a mild reducing agent. Huang and coworkers demonstrated that increasing the proportion of tryptophan in the peptide resulted in reduction of sodium tetrachloropalladate(II) and tight binding to the palladium surface (103).

The adoption of green chemistry techniques by the use of naturally occurring products as stabilisers for nanomaterials is also an area of huge potential. For example, Varma has used tea and coffee extract to stabilise nanoparticles of palladium and other precious metals (104). The polyphenols present in the caffeine act as an effective reducing and capping agent. The environmentally benign nature of the caffeine (its high water solubility, low toxicity and biodegradability) make this route highly desirable.

The use of stabilising agents with considerable steric bulk in order to prevent agglomeration has also been applied to resorcinarenes (105) and non-functionalised cyclodextrins (106). Analysis of palladium nanoparticles stabilised with 2-hydroxypropyl-α-cyclodextrin found that the cyclic oligosaccharide was only physisorbed onto the surface *via* hydrophobic interactions. This weak interaction resulted in the nanoparticles showing good yields and selectivities in Suzuki, Heck and Sonogashira reactions in neat water under low palladium loadings.

6. Conclusions

The utilisation of nanodimensional materials offers significant benefits in a range of different applications. In order to maximise their usefulness, reliable syntheses are required that can generate well-defined nanoparticles with a high degree of monodispersity. This aim is being achieved in the synthesis of palladium nanoparticles by using organic ligands, surfactants and sterically bulky molecules to control the synthesis. This enables properties such as the size, shape, solubility and surface functionality of the resulting nanoparticles to be carefully tuned. Such materials are being explored for many different applications, especially in catalysis, where palladium can effectively catalyse a range of different transformations.

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