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Nanoparticle Formation

Mechanism of Formation of Palladium Nanoparticles: Lewis Base Assisted, Low-Temperature Preparation of Monodisperse Nanoparticles**

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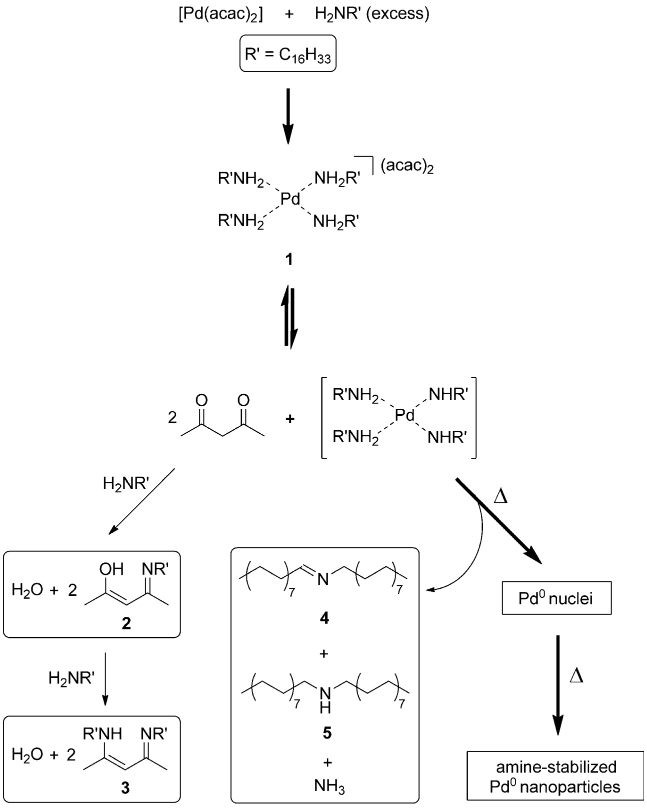
The applications of metal nanoparticles, which take advantage of the high surface to volume ratio, high reactivity, size, shape, and recyclability of these materials, continue to expand.[1] Palladium nanoparticles can serve as catalysts for Heck, Suzuki, and Sonagashira couplings, as well as hydrogenation and oxidation reactions.[2] In addition, the role of such nanoparticles in "homogeneous" Pd catalysis remains under debate.[3] Pd nanoparticles are often prepared by the reduction of Pd^{II} precursors in the presence of surface stabilizers such as amines,[4] phosphines,[5] thiols,[6] dendrimers,[7] or polymers;[8] however, the mechanism of nanoparticle formation is not known. Herein, we elucidate the mechanism by which Pd nanoparticles are formed in the presence of amines, and demonstrate that Lewis bases such as phosphine oxides or sulfoxides can act to significantly lower the temperature at which monodisperse nanoparticles form.



Scheme 1. Proposed mechanism for the formation of Pd^0 nanoparticles from $[Pd(acac)_2]$ and a primary amine.

The preparation of organic-soluble Pd nanoparticles often involves the thermolysis of a Pd^{II} precursor, such as $[Pd(acac)_2]$ (acac = acetylacetonate)[5a] or sodium tetrachloropalladate,[4b] in the presence of an amine, such as oleylamine. High temperatures (200–300 °C) and air-free conditions are necessary unless another reducing agent is introduced.[4c,9] In the presence of a coordinating additive, such as tri-*n*-octylphosphine[4b,5a] or 1-dodecanethiol,[4a] monodisperse nanoparticles can be obtained. We used ^{1}H NMR spectroscopy to elucidate the intermediates involved in the preparation of nanoparticles from $[Pd(acac)_2]$ in the presence of excess 1-hexadecylamine. Spectra were taken of aliquots removed at 10 °C increments as the reaction was heated (Supporting Information, Figure S1; see Table S1 for a complete list of the compounds identified). At low temperatures (ca. 50 °C) tetraaminopalladium salt **1** forms (Scheme 1), as evidenced by a diagnostic peak in the ^{1}H NMR spectrum corresponding to a Pd-bound NH_2 group ($\delta = 5.6$ ppm).[10] At much higher temperatures (ca. 130 °C), the mixture darkened significantly, $[Pd(acac)_2]$ was depleted, and acetylacetone (Hacac) and ketimine **2** were formed.[11] Ketimine **2** forms by condensation of Hacac with the amine.[12] The reaction of Na(acac) and 1-hexadecylamine does not result in the formation of any **2**, thus, protonation of $acac^-$ must occur first in order to form **2**. Here, Hacac can form from **1** by proton exchange between the Pd-bound amine ligands and the $acac^-$ in the outer coordination sphere, giving Hacac and a Pd–amido complex.[10,13] Hacac that is present at equilibrium can react with amine to give **2**, resulting in the formation of higher amounts of the putative amido complex. We do not directly observe the Pd–amido complex by ^{1}H NMR spectroscopy; it appears to be unstable and may form amido-bridged Pd clusters.[14]

It is known that Pd–alkylamido complexes readily undergo β-hydride elimination from the alkyl group to produce a Pd–hydride complex with a coordinated imine (Scheme 2).[14a,15] When $[Pd(acac)_2]$ and 1-hexadecylamine are reacted at 80 °C, a peak is observed in the ^{1}H NMR

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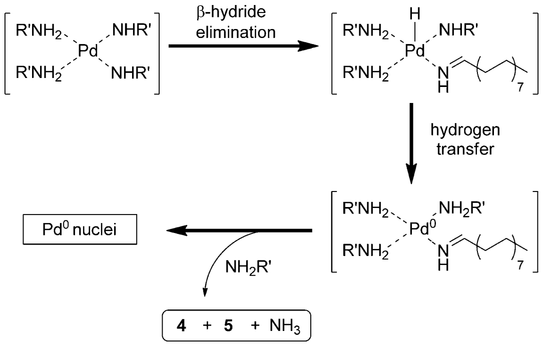
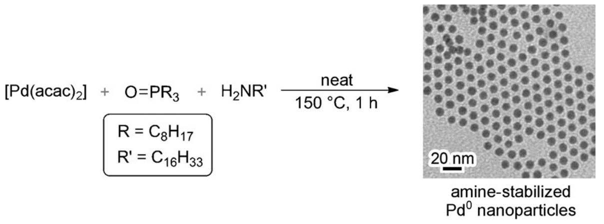


Scheme 2. Formation of Pd^0 by β-hydride elimination and hydrogen transfer.

spectrum of the mixture in $[D_8]$toluene at $\delta = -0.83$ ppm, which is attributed to a Pd–hydride complex (Figure S2).[16] Complexes of this type with a coordinated imine are unstable and generate Pd^0 upon heating, possibly from reductive elimination of hydride and an amide ligand to regenerate the primary amine.[17]

This mechanism suggests the possibility that the formation of nanoparticles can be facilitated by increasing the amount of amido complex formed. Lewis bases, such as phosphine oxides, are known to increase the nucleophilicity of amines,[18] thus the addition of a Lewis base is expected to increase the rate of formation of **2**, with the concomitant formation of more of the Pd–amido complex. Phosphine oxides coordinate weakly to late transition metals and have been only rarely used to stabilize metal nanoparticles,[19] although they have been used extensively to prepare quantum dots[20] and metal oxide nanoparticles.[21]

Upon addition of tri-*n*-octylphosphine oxide (TOPO) to a mixture of $[Pd(acac)_2]$ and 1-hexadecylamine, darkening of the solution occurred at a significantly lower temperature than in the absence of TOPO. At about 85 °C, the solution started to turn black (Figure S3), and the mixture became dark black by 150 °C, which is indicative of the presence of Pd^0. After cooling, a black precipitate, dispersible in organic solvents such as chloroform and hexanes, was isolated by centrifugation, and transmission electron microscopy (TEM) of the precipitate revealed highly monodisperse spherical nanoparticles (diameter $= [8.7 \pm 0.7]$ nm; Scheme 3).[22] The powder X-ray diffraction (PXRD) pattern of the nanoparticles shows broad signals corresponding to fcc Pd in the nanoscopic regime (JCPDS card no.:46-1043; Figure S4). Monodisperse Pd nanoparticles can be isolated using these conditions at temperatures as low as 85 °C (Figure S5), but at 60 °C, the particles are not as monodisperse as those prepared at higher temperatures (Figure S6). The Pd nanoparticles are highly catalytically active, as demonstrated by their use in a prototypical Suzuki–Miyaura cross-coupling reaction (see Table S2).



Scheme 3. Synthesis of amine-stabilized Pd nanoparticles in the presence of a phosphine oxide.

Solution ^{1}H NMR spectroscopy of the nanoparticles formed in the presence of TOPO indicates that the stabilizing agent is 1-hexadecylamine, with an upfield shift of the N$-$CH$_2$ protons and peak broadening observed owing to interaction of the amine with the nanoparticle surface (Figure S7). The FT-IR spectrum of the nanoparticles shows a broad N$-$H band and other bands close to those in the spectrum of 1-hexadecylamine (Figure S8). The ^{1}H NMR, ^{31}P NMR, and IR spectra show no indication of the presence of TOPO on the nanoparticles.

When the reaction mixture containing $[Pd(acac)_2]$, amine, and TOPO is slowly heated, the formation of ketimine **2** is observed at temperatures as low as 50 °C, in contrast to the reaction performed without TOPO (Figure S9). New peaks in the ^{1}H NMR spectrum attributed to the formation of diketimine **3** can be observed when the reaction mixture is heated to >130 °C. Diketimine **3** is formed by the condensation of **2** with another equivalent of the amine, possibly with TOPO as catalyst. Compound **3** appears to be the final destination of the acac ligand, as no further acac-based compounds can be identified in the temperature range studied.

Furthermore, additional organic compounds are formed during the formation of the nanoparticles. Aldimine **4** is observed by ^{1}H NMR spectroscopy at the same temperature that Pd nanoparticles begin to form.[23] Aldimines, such as **4**, are known intermediates in the Pd^0-catalyzed condensation of primary amines to form secondary amines.[24] Dialkylamine **5** was also observed in the ^{1}H NMR spectrum of the reaction mixture,[25] although dialkylamine was not observed on the nanoparticles as stabilizer, presumably owing to the stronger Lewis basicity of the primary amine.[26] It is likely that the coordinated imine resulting from β-hydride elimination undergoes nucleophilic attack by a primary amine to give aldimine **4**, dialkylamine **5**, and NH_3.[27]

Monitoring the reaction of $[Pd(acac)_2]$ and 1-hexadecylamine at 80 °C shows that the presence of TOPO results in more rapid formation of ketimine **2** (Figure S10–12). TOPO also affects the rate of formation of **2** from Hacac (Figure S13), supporting the conclusion that the phosphine oxide acts to increase the nucleophilicity of the amine towards Hacac. Given that formation of **2** is enhanced in the presence of TOPO, it is logical that faster depletion of Hacac in the presence of TOPO will generate more Pd–amido complex, thus lowering the temperature of nanoparticle formation. The formation of Pd^0 can be observed at <95 °C with the addition of 10 mol % of TOPO, which is consistent with this compound acting in a catalytic role, although the nanoparticles prepared under these conditions were not monodisperse (Figure S14). This result suggests that the amount of TOPO present is important in controlling the monodispersity of the nanoparticles, possibly by affecting the rate of the side reactions it is involved in and by influencing the nucleation of Pd^0. It is possible that TOPO also acts in other ways, for example, the possibility that TOPO facilitates the proton transfer from **1** to outer sphere acac$^-$ cannot be eliminated. Monitoring the ^{31}P NMR spectra during these reactions shows only a signal corresponding to TOPO, with no additional signals observed, confirming that TOPO does not serve as a capping agent and does not coordinate to form stable complexes with Pd.

When the reaction is conducted without 1-hexadecylamine ([Pd(acac)$_2$] and TOPO only), Hacac is formed, but does not react further (Figure S15). A relatively unstable Pd complex results and is reduced at lower temperature than when an amine is present, but monodisperse nanoparticles are not formed under these conditions (in the absence of a stabilizing group).

These results suggest that other Lewis bases could also act to facilitate Pd nanoparticle formation. When dimethylsulfoxide (DMSO) was used in place of TOPO with [Pd(acac)$_2$] and 1-hexadecylamine, nanoparticles were formed starting at about 100 °C, although these particles were not as monodisperse as when TOPO was used (Figure S16). It is possible that the less Lewis basic DMSO is not as effective at increasing the nucleophilicity of the amine, thus resulting in a higher temperature for formation of Pd^0. Using a different amine, oleylamine, in the reaction as a stabilizing agent also gives monodisperse nanoparticles (Figure S17), demonstrating that the effect of TOPO is not limited to the use of 1-hexadecylamine.

In summary, we have shown that Pd nanoparticles are formed from [Pd(acac)$_2$] by proton transfer from the initially formed tetraaminopalladium salt **1** to acac$^-$ to yield a putative amido complex. This reacts further by β-hydride elimination and hydrogen transfer to give a Pd^0 species by eliminating aldimine **4** and dialkylamine **5**. Adding Lewis bases, such as TOPO and DMSO, reduces the temperature at which highly monodisperse nanoparticles are formed. This shows that Pd nanoparticles can readily form at low temperatures from a Pd^{II} precursor, which suggests that caution is warranted in the interpretation of homogeneous catalysis studies involving amines and Lewis bases as reagents. In addition to providing insight into the mechanism, the identification of organic byproducts **2**–**5** is important, as these compounds may be present when [Pd(acac)$_2$] is used as a catalyst, or when Pd nanoparticles are formed in the presence of amines. Studies to explore the relevance of the mechanism elucidated here to other Pd precursors, and the preparation of other noble metal nanoparticles are underway.

Experimental Section

The TOPO assisted preparation of monodisperse hexadecylamine stabilized Pd^0 nanoparticles was performed using standard Schlenk techniques. A three-necked round-bottom flask was charged with [Pd(acac)$_2$] (0.021 g, 0.067 mmol), 1-hexadecylamine (0.79 g, 3.3 mmol), and tri-*n*-octylphosphine oxide (0.88 g, 2.3 mmol). A thermocouple was inserted through the side-arm of the round-bottom flask, and the solids were subjected to three vacuum/nitrogen cycles. After backfilling the system with nitrogen, the reaction mixture was heated at a rate of 3.3 °C min^{-1} to 150 °C, and held at this temperature for 1 h. The reaction mixture melted in the course of the reaction to form a light yellow oil, and turned black at ca. 85 °C. After cooling, the nanoparticles were rinsed three times with EtOH (20 mL) and isolated as a black solid by centrifugation.

See the Supporting Information for details on other experiments.

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