



Selective synthesis of nanosized palladium phosphides from white phosphorus

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The reaction of white phosphorus with the palladium(0) complex [Pd₂(dba)₃] (dba is dibenzylideneacetone) leads to stable associates [Pd(P₄)]_n. The coordination polymer obtained is stabilized in a solid state *via* the formation of nanosized palladium phosphides Pd₃P₂ and Pd₆P with average particle sizes of 140 and 65 nm, respectively.

The advance of nanotechnology requires new effective processes for the selective preparation of nanosized associates.¹ In this context, the relationship between the size and properties of the resulting particles attracts special attention.

Transition metal phosphides are important since they are widely used in catalysis, magnetochemistry and biomedicine.^{2–6} Nanosized palladium phosphides are of interest for organic synthesis due to their high activity in hydrogenation processes.⁷ Solvothermal synthesis^{1,8} is the most common method for the preparation of nanocrystalline transition-metal phosphides. This method is based on the interaction of sodium phosphides and transition metal salts in benzene at 150–200 °C. As a result, FeP,⁹ CoP/Co₂P¹⁰ and Ni₂P¹¹ nanoparticles can be synthesized. Another method includes interaction between highly reactive phosphines, like tris(trimethylsilyl)phosphine, with metal salts or complexes in the presence of a coordinating solvent (trioctylphosphine oxide or trioctylphosphine), which prevents the aggregation of nucleating phosphide particles by coordination to the surface of the growing particle. These high-boiling solvents made it possible to perform reactions at temperatures up to 350 °C to enhance the crystallinity of nanoparticles. As a consequence, FeP, MnP, PtP₂, Rh₂P, Au₂P₃, Pd₃P₂ and PdP₂ were synthesized.^{1,8} Using methods, which involve trialkoxysilane-functionalized phosphine complexes and a silicon sol, Fe₂P, RuP, Co₂P, Rh₂P, Ni₂P, Pd₄P₂ and PtP₂ were prepared.¹

White phosphorus[†] is the major source for the preparation of organophosphorus compounds,¹² whereas its reactions with a variety of chemical elements lead to inorganic phosphides.^{3,13} Nanosized transition metal phosphides have been prepared directly from white phosphorus.^{1,7,13–15} For example, nanosized palladium phosphides PdP₂, Pd₄P₂, Pd₅P₂ and Pd₆P have been obtained under various conditions.^{7,8,16,17} It was postulated⁷ that PdP₂ and Pd₅P₂ are intermediates on the way to the formation of Pd₆P.

[†] White phosphorus and palladium phosphides are hazardous compounds. White phosphorus is highly toxic and inflammable. In an emergency, white phosphorus can be treated with an aqueous copper sulfate solution or sand. Getting on the skin, white phosphorus gives strong painful long time not healing burns. Continuous breathing of white phosphorus vapor results in disease of the bone tissue, loss of the teeth and necrosis of the parts of jaw. White phosphorus should be stored under water in well airing dark place. In case of the skin burn, to wash out by a dilute aqueous solution of KMnO₄ or CuSO₄. An aqueous copper sulfate solution (2%) can be used as an antidote upon poisoning. All of the reactions and handling of phosphines and white phosphorus should be carried out under an inert atmosphere in a well-ventilated hood.

The aim of this work was to investigate the mechanism and stoichiometry of the interaction between white phosphorus and tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃] and to characterize the formed nanosized palladium phosphides.

The interaction of white phosphorus with [Pd₂(dba)₃] was studied by ³¹P NMR spectroscopy, atomic force microscopy (AFM) and inductively coupled plasma mass spectrometry (ICP MS).

The addition of a white phosphorus solution in THF to a dark-red solution of [Pd₂(dba)₃] in THF leads to decoloration of the solution and the formation of black amorphous precipitate that becomes crystalline during long-term stirring.[‡] The supernatant becomes slightly dark-green. The ³¹P NMR monitoring shows no signal corresponding to white phosphorus when reagents are mixed in the molar ratio Pd:P₄ = 1:1 {[Pd₂(dba)₃]:P₄ = 1:2} or when [Pd₂(dba)₃] is in an excess. However, there is a signal of white phosphorus, –525.5 ppm (s), in the ³¹P NMR [161.9 MHz, THF (C₆D₆ capillary), 25 °C] spectra of the reaction mixture when a small excess of white phosphorus was added. Note that the supernatant does not contain any phosphorus product according to NMR data. Moreover, the dark-green color of the supernatant

[‡] The experiments were carried out under dry nitrogen using a standard Schlenk system. THF and diethyl ether were purified by distillation from Na/benzophenone. DMF was dried by calcium hydride and distilled (three times) *in vacuo*. White phosphorus was purified with a solution of potassium dichromate in concentrated H₂SO₄ followed by recrystallization from DMF. The resulting phosphorus was melted (50 °C) in DMF and rolled into beads while stirring with a magnetic bar and then cooling. White phosphorus was stored under water in a dark place and washed sequentially in ethanol, acetone and diethyl ether. Commercial [Pd₂(dba)₃] (Alfa Aesar) was used without additional purification.

The ³¹P (161.9 MHz) and ¹H (400.1 MHz) NMR spectra were recorded using a Bruker-400 instrument at 25 °C. The concentrations of palladium and phosphorus in powder were determined by ICP MS on an Elan DRC II mass spectrometer (PerkinElmer). Quantitative analysis was performed by dissolving a 10 mg sample in concentrated nitric acid (0.2 ml). Then, deaerated water was added to a volume of 50 ml. The maximum calculation error was no higher than ±10%.

A MultiMode V atomic force microscope was used to investigate the morphology of the particles. The 250–350 kHz cantilevers (Veeco) with silicon tips were used in the measurements. The microscopic images were obtained by means of a 8279JV scanner with a 256×256 resolution. The scanning rate was 1 Hz. An antivibrational system (SG0508) was used to eliminate external distortions. The dispersion of the investigated particles was placed on a mica surface with the roughness of no more than 1–5 nm. The surface was scanned after the evaporation of solvent (THF).