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Selective synthesis of nanosized palladium phosphides from white phosphorus

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The reaction of white phosphorus with the palladium(0) complex [$Pd_2(dba)_3$] (dba is dibenzylideneacetone) leads to stable associates [$Pd(P_4)$]$_n$. The coordination polymer obtained is stabilized in a solid state *via* the formation of nanosized palladium phosphides Pd_3P_2 and Pd_6P 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/Co_2P[10] and Ni_2P[11] 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, PtP_2, Rh_2P, Au_2P_3, Pd_5P_2 and PdP_2 were synthesized.[1,8] Using methods, which involve trialkoxysilane-functionalized phosphine complexes and a silicon sol, Fe_2P, RuP, Co_2P, Rh_2P, Ni_2P, Pd_4P_2 and PtP_2 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 PdP_2, Pd_4P_2, Pd_5P_2 and Pd_6P have been obtained under various conditions.[7,8,16,17] It was postulated[7] that PdP_2 and Pd_5P_2 are intermediates on the way to the formation of Pd_6P.

The aim of this work was to investigate the mechanism and stoichiometry of the interaction between white phosphorus and tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$] and to characterize the formed nanosized palladium phosphides.

The interaction of white phosphorus with [$Pd_2(dba)_3$] was studied by ^{31}P 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 [$Pd_2(dba)_3$] 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 ^{31}P NMR monitoring shows no signal corresponding to white phosphorus when reagents are mixed in the molar ratio $Pd:P_4 = 1:1$ {$[Pd_2(dba)_3]:P_4 = 1:2$} or when [$Pd_2(dba)_3$] is in an excess. However, there is a signal of white phosphorus, –525.5 ppm (s), in the ^{31}P NMR [161.9 MHz, THF (C_6D_6 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

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[†] 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 a 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 $KMnO_4$ or $CuSO_4$. 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 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 H_2SO_4 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 [$Pd_2(dba)_3$] (Alfa Aesar) was used without additional purification.

The ^{31}P (161.9 MHz) and ^{1}H (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 silicone 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).

indicates the total conversion of the initial $[Pd_2(dba)_3]$ complex in solution. The ^1H NMR spectra of the supernatant show signals corresponding to free dba, which remains in solution. Therefore, the reaction of white phosphorus and $[Pd_2(dba)_3]$ leads to degradation of the complex since white phosphorus is a good ligand for palladium coordination centres. Thus, we can conclude that at the molar ratio $Pd:P_4 = 1:1$ $\{[Pd_2(dba)_3]:P_4 = 1:2\}$ white phosphorus is fully converted into insoluble black precipitate, which is formed by the degradation of the initial $[Pd_2(dba)_3]$ complex.

An additional heating of the reaction mixture up to 60 °C with continuous stirring allowed us to increase the solubility of the formed compound and, according to ^{31}P NMR, only one phosphorus product with the chemical shift δ_P –462.3 ppm was observed in the reaction mixture (Figure 1). The chemical shift in a very high field and the absence of signal coupling (also when ^{31}P NMR spectra were recorded with a phosphorus decoupling function) suggest that all of the four phosphorus atoms are equivalent and belong to an intact P_4 tetrahedron.[18] We found that such an interaction resulted in formation of $[Pd(P_4)]_n$ coordination polymer, in which P_4 tetrahedrons are bound to palladium(0) atoms by coordination bonds [reaction (1)].

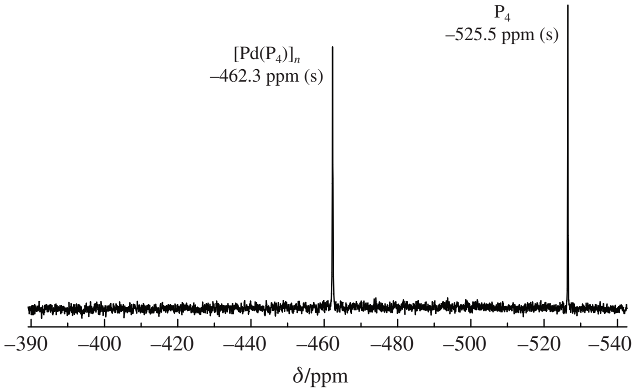

Figure 1 ^{31}P NMR spectrum [161.9 MHz, THF (C_6D_6 capillary), 25 °C] of the solution containing white phosphorus [δ –525.5 ppm (s)] and coordination polymer $[Pd(P_4)]_n$ [δ –462.3 ppm (s)].

$$n[Pd_2(dba)_3] + 2nP_4 \rightarrow 2[Pd(P_4)]_n + 3n(dba) \qquad (1)$$

Such a stoichiometry was also demonstrated by titration of the $[Pd_2(dba)_3]$ complex with a white phosphorus solution. The ability of the formed coordination polymer to eliminate free P_4 molecules when the precipitate is heated up to 60 °C *in vacuo* (10^{-6} Torr) confirms that the precipitate consists of white phosphorus molecules coordinated to palladium. Note that white phosphorus traces were found in a cooling trap (N_2 liquid). The coordination polymer is relatively stable in solution and involved in the ligand exchange dynamic processes resulting in ^{31}P NMR signal broadening after stirring the solution for 2 h.

The oxidation of palladium(0) to palladium(II) was not observed analogously to data reported[15] for indium and zinc complexes. The reaction of white phosphorus with In and Zn is a redox one accompanied by the opening of the P_4 tetrahedron with the formation of nanosized indium and zinc phosphides [reaction (2)].[15]

$$6Zn^0_{(met)} + P_4 \rightarrow 2Zn_3P_2 \qquad (2)$$

The reactivity of the synthesized coordination polymer differed from that of metal phosphides where phosphorus has the oxidation state of –3. Thus, Zn and Pd phosphides react with water with the formation of PH_3 and H_3PO_3, respectively. Note that the formation of H_3PO_3 was mentioned for Group VIII transition metal complexes bearing intact P_4 molecules in the coordination sphere.[19–21]

Our attempts to isolate the coordination polymer $[PdP_4]_n$ as a solid material failed. The precipitate was filtered off, washed with diethyl ether and dried. Black crystalline powder was isolated, which has the formula Pd_3P_2 according to elemental analysis, and an average size of 140 nm determined by AFM analysis (Figure 2).

The drying of the precipitate in a high vacuum (10^{-6} Torr) at 60 °C led to the loss of phosphorus and the selective formation of stable nanosized palladium phosphides like Pd_6P. According to AFM analysis, Pd_6P is a homogeneous sample with an average particle size of 65 nm (Figure 3), which is much smaller than that of Pd_3P_2.

The supernatant consists of only one phosphorus-containing compound, phosphorous acid H_3PO_3 [^{31}P NMR, 161.9 MHz, THF (C_6D_6 capillary), 25 °C: δ 2.7 ppm (d, $^1J_{PH}$ 667 Hz)], when a small amount of deaerated water was added to a THF suspension of

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Synthesis of coordination polymer $[Pd(P_4)]_n$. 0.1600 g (0.175 mmol) of $[Pd_2(dba)_3]$ was dissolved in 15 ml of THF by stirring for 30 min. Then, 2.9 ml of a white phosphorus solution (0.12 mol dm^{-3}) in THF containing 0.350 mmol of P_4 was added dropwise at 20 °C. Immediately, the black precipitate was formed in the reaction mixture. The reaction mixture was heated to 60 °C and stirred for 15 min. After cooling to room temperature and precipitation for 2 h, the supernatant was analyzed by ^{31}P NMR spectroscopy showing presence of the coordination polymer $[Pd(P_4)]_n$. Then, the slightly green supernatant was decanted and the precipitate was washed with diethyl ether (3×10 ml). After drying the isolated precipitate *in vacuo* at 20 °C, it was identified as the palladium phosphide Pd_3P_2. According to AFM analysis, the average size of the formed particles is 140 nm. The yield of Pd_3P_2 was 0.035 g (79%). The evacuation (10^{-6} bar) of the resulting product at 60 °C led to the formation of the palladium phosphide Pd_6P with an average particle size of 65 nm. The yield of Pd_6P was 0.024 g (62%). ^{31}P NMR (THF, C_6D_6 capillary) δ: –462.3 (s, $[Pd(P_4)]_n$). Found (%): P, 16.29; Pd, 83.70. Calc. for Pd_3P_2 (381.21) (%): P, 16.25; Pd, 83.75. Found (%): P, 4.59; Pd, 95.40. Calc. for Pd_6P (669.49) (%): P, 4.63; Pd, 95.37.

Preparation of palladium phosphide Pd_3P_2. 0.1767 g (0.193 mmol) of $[Pd_2(dba)_3]$ was dissolved in 15 ml of THF by stirring for 30 min. Then, 3.2 ml of a white phosphorus solution (0.12 mol dm^{-3}) in THF containing 0.386 mmol of P_4 was added dropwise. Immediately, a black precipitate was formed in the reaction mixture. After stirring the solution for 30 min, the reaction mixture was allowed to stand for 12 h resulting in the formation of a black precipitate and a slightly green clean supernatant. The precipitate isolated by the decantation of the supernatant was washed with diethyl ether (3×10 ml) and dried *in vacuo* (10^{-6} bar) at 20 °C leading to nanosized palladium phosphide Pd_3P_2 with an average size of 140 nm. Yield, 0.042 g (86%). Found (%): P, 16.28; Pd, 83.69. Calc. for Pd_3P_2 (381.21) (%): P, 16.25; Pd, 83.75.

Preparation of palladium phosphide Pd_6P. Method 1. 0.1026 g (0.112 mmol) of $[Pd_2(dba)_3]$ was dissolved in 10 ml of THF by stirring for 30 min. Then, 1.9 ml of a white phosphorus solution (0.12 mol dm^{-3}) in THF containing 0.224 mmol of P_4 was added dropwise. Immediately, a black precipitate was formed in the reaction mixture. After stirring the solution for 2 h and further precipitation for 12 h, a black precipitate in a slightly green supernatant was obtained. The precipitate was isolated by careful decantation of the supernatant, washed with diethyl ether (3×10 ml) and dried *in vacuo* (10^{-6} bar) at 60 °C leading to nanosized palladium phosphide Pd_6P with an average size of 65 nm. Yield, 0.020 g (80%). Found (%): P, 4.65; Pd, 95.29. Calc. for Pd_6P (669.49): P, 4.63; Pd, 95.37. *Method 2.* 0.2637 g (0.288 mmol) of $[Pd_2(dba)_3]$ was dissolved in 10 ml of THF by stirring for 30 min. Then, 0.2 ml of a white phosphorus solution (0.12 mol dm^{-3}) in THF containing 0.024 mmol of P_4 was added dropwise. Immediately, a black precipitate was formed in the reaction mixture. After stirring the solution for 2 h and further precipitation for 12 h, a black precipitate in a bright reddish supernatant was obtained. The precipitate was isolated by careful decantation of the supernatant, washed with diethyl ether (3×10 ml) and dried *in vacuo* (10^{-6} bar) at 20 °C leading to nanosized palladium phosphide Pd_6P with an average size of 65 nm. Yield, 0.056 g (87%). Found (%): P, 4.62; Pd, 95.35. Calc. for Pd_6P (669.49) (%): P, 4.63; Pd, 95.37.

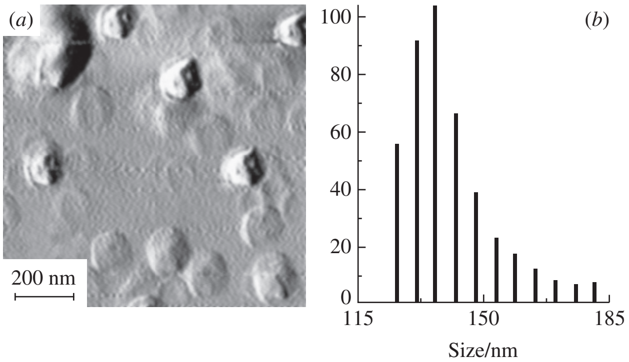

Figure 2 (*a*) AFM image and (*b*) particle size distribution of $\mathrm{Pd_3P_2}$.

palladium phosphide $\mathrm{Pd_3P_2}$ or $\mathrm{Pd_6P}$. The process is accompanied by the formation of molecular hydrogen [^{1}H NMR, 400.1 MHz, THF ($\mathrm{C_6D_6}$ capillary), 25 °C: δ 4.6 ppm (s)]. Similar reactivity of white phosphorus saturated by $[\mathrm{Pd_2(dba)_3}]$ towards water with the formation of molecular hydrogen was observed earlier.[22] According to published data,[14,22] phosphorous acid is formed as a result of the hydrolysis of a white phosphorus tetrahedron in the coordination sphere of a palladium(0) complex [reaction (3)].

$$[\mathrm{Pd(P_4)}]_n + 12n\,\mathrm{H_2O} \rightarrow n\,\mathrm{Pd_{(met)}} + 4n\,\mathrm{H_3PO_3} + 6n\,\mathrm{H_2} \qquad (3)$$

Thus, we can conclude that the reaction of white phosphorus with $[\mathrm{Pd_2(dba)_3}]$ is not a simple redox reaction. It is a complex process leading to the formation of a coordination polymer where white phosphorus molecules display a multidentate coordination behavior. The formation of phosphorous acid results from catalytic hydrolysis involving the cleavage of all P–P bonds in a white phosphorus tetrahedron in the coordination sphere of palladium(0).

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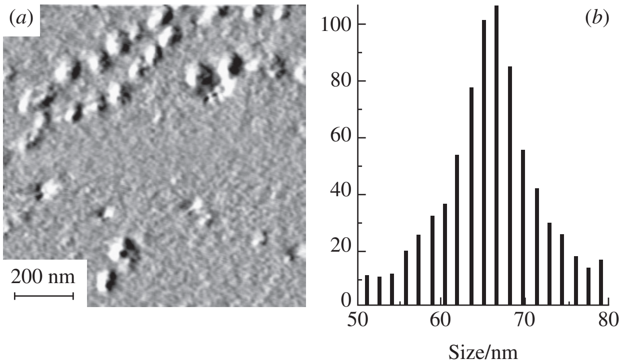

Figure 3 (*a*) AFM image and (*b*) particle size distribution of $\mathrm{Pd_6P}$.

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