Activation and transformation of white phosphorus by palladium(II) complexes*

*R. M. Kagirov,[a] A. V. Voloshin,[b] I. Kh. Rizvanov,[a] O. G. Sinyashin,[a] and D. G. Yakhvarov[a]**

[a]A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843) 273 2253. E-mail: yakhvar@iopc.ru
[b]Kazan State University,
18 ul. Kremlevskaya, 420008 Kazan, Russian Federation

A reaction of bis(triphenylphosphine)palladium dibromide with white phosphorus in the presence of $NaBPh_4$ selectively gives phosphorous acid H_3PO_3. The mechanism of the formation involves coordination of a white phosphorus molecule, ligand exchange, and hydrolysis of the coordinated P_4 molecule in the coordination sphere of palladium.

Key words: white phosphorus, palladium complexes, phosphorous acid.

Development of new technological approaches to the synthesis of organophosphorus compounds (OPC) directly from white phosphorus is a key problem of contemporary organophosphorus chemistry. Metal complex catalysis is a highly efficient alternative of the environmentally hazardous preparation of OPC from white phosphorus through phosphorus chlorides (chlorine technology).[1] However, catalytic conversion of all the four phosphorus atoms in the P_4 molecule into the target product still remains an unsolved problem.[2]

Much research has been focused on the study of the reactivity of white phosphorus toward various metal complexes.[3,4] The research mainly deals with the synthesis of metal complexes containing fragments P_n (n = 2—14) resulting from the degradation of the P_4 molecule or from the recombination of small fragments into polyatomic aggregates.[5,6] At the same time, metal complexes containing a coordinated white phosphorus molecule (P_4) are studied much more poorly.[7—10]

It should be noted that the literature data on the reactivities of palladium complexes in the coordination and transformation of white phosphorus are scarce.[1] According to previous data,[11] palladium salts promote the oxidation of white phosphorus with such oxidants as $CuCl_2$, $NaNO_2$, and $FeCl_3$.

In the present work, we demonstrate that reactions of molecular white phosphorus with cationic palladium complexes containing labile ligands in the coordination sphere give phosphorous acid as the major product, which is due to coordination and subsequent degradation of the tetrahedron P_4. We found that the formation of H_3PO_3 in the coordination sphere of palladium complexes results from the hydrolysis of the coordinated P_4 molecule, passing through the complex intermediates $[Pd_x(P(OH)_3)_y]$.

Results and Discussion

When we directly mixed the starting complex bis(triphenylphosphine)palladium dibromide and white phosphorus in THF, no reaction occurred (^{31}P NMR data at ~20 and 60 °C). The ^{31}P NMR spectrum of the reaction mixture shows only the signals for white phosphorus (δ 526.88) and the starting complex $[(PPh_3)_2PdBr_2]$ (δ 23.88). At the same time, it is known[1] that a white phosphorus molecule can, like phosphines, act as a ligand to Group VIII transition metals. This is usually achieved by employing cationic complexes of transition metals with uncoordinated anions that allow the tetrahedron P_4 to have access to the vacant orbital of the metal.[1] That is why we generated cationic palladium complexes in the presence of a stoichiometric amount of $NaBPh_4$, which favors removal of the bromide ions from the coordination sphere of the complex $[(PPh_3)_2PdBr_2]$ (Scheme 1). As a result, the bright yellow solution turned light orange.

When a solution of white phosphorus in THF was added to the above solution of the complex, the resulting solution changed color even at 20 °C and produced a black precipitate that is well soluble in DMF and DMSO but is insoluble in most other organic solvents.

Monitoring of the reaction by ^{31}P NMR spectroscopy revealed that the addition of white phosphorus releases free PPh_3 in solution (δ −5.65). Therefore, white phosphorus initiates ligand exchange so that triphenylphosphine molecules are displaced from the coordination

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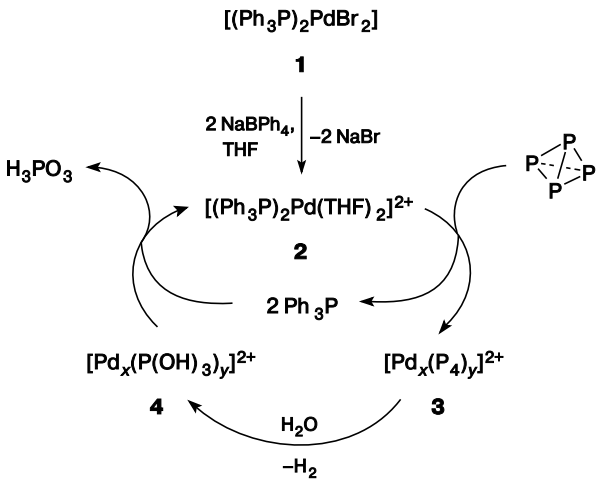
Scheme 1



sphere of the palladium complex. This is primarily due to the fact that a coordinated white phosphorus molecule substantially increases the electron density on the central metal atom, which weakens the coordination bond between palladium and triphenylphosphine and facilitates the release and exchange of the latter for white phosphorus. These exchange interactions between PPh_3 and white phosphorus in the coordination sphere of palladium are confirmed by the broadened signal of free PPh_3 in the ^{31}P NMR spectrum.

According to elemental analysis data, the black precipitate contains palladium phosphides with a molar P : Pd ratio of 5 : 2; no other phosphorus compounds were detected in the reaction mixture. However, after a small amount of deaerated water was added and the resulting solution was stirred in an inert atmosphere for 24 h, the supernatant contained phosphorous acid as the major product (^{31}P NMR, δ: 2.70, d, $^1J_{P,H}$ = 667 Hz). The minor products included H_3PO_4 (δ 0.00) and $H_4P_2O_7$ (δ 4.46). The latter was completely converted into H_3PO_4 upon addition of a small amount of 2 *N* aqueous HCl to the reaction mixture. We found that the formation of H_3PO_3 results from hydrolysis of the coordinated white phosphorus molecule in the coordination sphere of palladium. Earlier,[12,13] this has been noted for some complexes of Group VIII metals.

The MALDI mass spectrum of the supernatant contains the ion peaks with *m/z* 892 and 630 corresponding to the molecular ions $[Pd(PPh_3)_3]^+$ and $[Pd(PPh_3)_2]^+$, respectively. This confirms the structures of the complexes $[Pd(PPh_3)_3]$ and $[Pd(PPh_3)_2]$ in solution, with palladium in the zero oxidation state. Therefore, the oxidation of white phosphorus into phosphorous acid is accompanied by the partial reduction $Pd^{II} \rightarrow Pd^0$. The latter palladium remains in solution because of its recoordination by free PPh_3 present in the reaction mixture, which is evident from ^{31}P NMR data. We found that the formation of H_3PO_3 from white phosphorus in the presence of cationic palladium complexes with PPh_3 is a catalytic process activated by PPh_3 molecules released from cationic complex **2** (see Scheme 1).

Thus, the reactions of cationic palladium(II) complexes with white phosphorus involve coordination of the P_4 molecule followed by hydrolysis to phosphorous acid as the major product.

Experimental

All experiments were carried out under dry nitrogen in standard Schlenk ware. Freshly distilled solvents were used; THF was distilled over Na/benzophenone. White phosphorus was purified with a solution of potassium bichromate in conc. H_2SO_4 followed by recrystallization from DMF. The resulting phosphorus was melted (50 °C) and rolled into beads while stirring with a magnetic bar and then cooling. Tributylphosphine oxide used as the internal standard for determination of the concentrations of the components in solution was prepared by oxidation of Bu_3P with a twofold excess of H_2O_2 in toluene at 20 °C. The complex $[(PPh_3)_2PdBr_2]$ was synthesized as described earlier.[14] $NaBPh_4$ (Across Organics) was employed as purchased.

^{31}P NMR spectra were recorded on a Bruker Avance-400 high-resolution spectrometer (161.9 MHz) in THF at ~20 °C. MALDI mass spectra were recorded on a Bruker Daltonics ULTRAFLEX III MALDI-TOF/TOF mass spectrometer with the *trans*-2-[3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]-malononitrile (DCTB) matrix. The palladium and phosphorus contents of the precipitates obtained were determined using inductively coupled plasma mass spectrometry (ICP-MS) on a Perkin—Elmer Elan DRC II mass spectrometer (USA) and atomic absorption spectroscopy (AAS) on a Carl Zeiss AAS1 spectrometer.

To confirm the formation of H_3PO_3 and H_3PO_4, small amounts of these acids were added to the reaction mixture and their concentrations were determined from the increased integral intensities of the corresponding signals in the ^{31}P NMR spectrum.

Reaction of the complex $[(PPh_3)_2PdBr_2]$ with white phosphorus. Sodium tetraphenylborate (0.0164 g, 0.048 mmol) was added to a solution of $[(PPh_3)_2PdBr_2]$ (0.019 g, 0.024 mmol) and Bu_3PO (0.01 g, 0.048 mmol) as the internal standard in THF (5 mL). The mixture was stirred at 50 °C for 1 h. The ^{31}P NMR spectrum (THF) of the mixture exhibited a signal at δ 27.57 due to the cationic complex $[(PPh_3)_2Pd(THF)_2]^{2+}$. Then a 0.06 *M* solution of white phosphorus (0.4 mL) in THF (Pd : P_4 = 1 : 1) was slowly added dropwise and the reaction mixture was stirred at 50 °C for 1 h. Deaerated water (2 μL) was added to the resulting solution. The ^{31}P NMR spectrum (THF) of the solution showed the signals of $H_4P_2O_7$ (δ 4.46), H_3PO_3 (δ 2.70, d, $^1J_{P,H}$ = = 667 Hz), and H_3PO_4 (δ 0.00) with an integral intensity ratio of 1 : 3 : 1, respectively.

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