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Convenient synthesis of μ-nitridobis(triphenylphosphonium) chloride ([PPN]Cl) with contribution of PCl_5 as chlorinating (PCl_5+PPh_3) or deoxygenating (PCl_5+OPPh_3) reagent

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Abstract

A convenient synthesis of μ-nitrido(triphenylphosphonium) chloride consisting of chlorination of PPh_3 by PCl_5 in 1,1,2,2-tetrachloroethane followed by the reaction with PPh_3 and $NH_2OH \cdot HCl$ is discussed. A possibility of obtaining [PPN]Cl as a result of deoxygenation of $OPPh_3$ using the same PCl_5, and subsequent reaction of the resultant product with PPh_3 and $NH_2OH \cdot HCl$ is shown.

Introduction

At present salts of the μ-nitridobis(triphenylphosphonium) cation (standard abbreviation [PPN]Cl) with various inorganic, complex and organometallic anions are widely used in chemistry. Interest in the compounds of the [PPN]X type is due to the following factors.

(i) Cation hydrophobycity. This factor to a large extent determines the solubility of [PPN]X salts in organic solvents including poorly solvating ones such as halogenalkanes (in particular CH_2Cl_2) [1–3].

(ii) Ability of $[PPN]^+$ cation to stabilize organometallic anions in solution and in the solid phase [4, 5].

(iii) [PPN]X salts serve as sources of X^- ions for anionic reactions in non-aqueous media [6, 7] and are also used in phase-transfer catalysis [8].

(iv) Salts with the $[PPN]^+$ cation are usually well crystallized and often provide single-crystals suitable for X-ray structure analysis (see, for example, refs. 9–12).

(v) The use of salts with the $[PPN]^+$ cation in catalysis [13–16].

(vi) The use of [PPN]X salts for extraction of complexes [17].

This paper deals with a convenient [PPN]Cl synthesis which can easily be carried out under laboratory conditions.

Experimental

μ-Nitridobis(triphenylphosphonium) chloride

A magnetic stirrer is placed into a three-necked round-bottomed flask with a thermometer and a system for distillation (connecting adapter, condenser, vacuum adapter and round-bottomed flask). It is filled with the triphenylphosphine solution (78.6 g, 0.30 mol) in 150 ml of 1,1,2,2-tetrachloroethane. Within 20–30 min on stirring finely powdered PCl_5 (43.7 g, 0.21 mol) is added to the mixture and the temperature is increased to 40–50 °C. After the addition of PCl_5 the mixture is heated to 110–115 °C for 15–20 min. At this temperature stirring is continued for about 20 min and the resultant PCl_3 can be distilled (10–12 ml, identified by its boiling point; PCl_3 can be removed at a much lower temperature when the system is connected with a vacuum line). After distillation the mixture is cooled to 50–60 °C, the connecting adapter is replaced by a reflux condenser connected with an H_2SO_4 drying system. At this temperature $NH_2OH \cdot HCl$ (7.30 g, 0.105 mol) is added to the mixture within 10 min. Then the mixture is heated with stirring and boiled for 8 h. The obtained homogeneous brownish solution is

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cooled to 20–25 °C and poured into 700 ml of hexane; the solvent is decanted in 15 min and the oily residue of 3 × 50 ml of hexane is washed out. The resultant substance is commonly crystallized within 1–2 min over 300 ml of an ethylacetate hexane mixture (1:5 by volume). The precipitate is filtered, washed on a filter with 3 × 50 ml of ethylacetate and 3 × 50 ml of hexane, and dried in air at 20 °C. As a result 50.7 g of the $[PPN]^+$ salt (product A) are obtained. The resultant substance is dissolved in a minimal amount of hot (80–90 °C) water, filtered, and concentrated HCl (ρ 1.18 g cm^{-3}) is added to the filtrate till the precipitation of a colorless substance is complete. The suspension is cooled to 20–25 °C, the precipitate is filtered, washed on a filter with 3 × 15 ml HCl and 3 × 50 ml of water, and dried in air at 20–25 °C. Yield of [PPN]Cl = 41 g, 72%.

Anal. Calc. for $C_{36}H_{30}ClNP_2$: Cl 6.18; N 2.44. Found: Cl 6.13; N 2.23%. Melting point (m.p.) (Kofler tables) 274–275 °C (lit. 268–270 °C [18]; 271–273 °C [19]). δ (^{31}P NMR) 21.1 ppm (in $CHCl_3$, 85% H_3PO_4 ext.); lit. 22.3 ppm [18]. Molar conductivity 71 ohm^{-1} mol^{-1} cm^2 in DMF. The IR spectra parameters and R_f values on TLC for [PPN]Cl samples synthesized with PCl_5 and with Cl_2 [18] are identical.

If HNO_3 or HBr are added to product A (*vide supra*) instead of HCl then $[PPN](NO_3)$ (m.p. 224–225 °C; lit. 224–225 °C [18]) or [PPN]Br (m.p. 253–255 °C; lit. 253–254 °C [20]) are isolated in the solid phase with a very good yield.

Results and discussion

Commonly [PPN]Cl [21–23] is used as a starting material for the synthesis of various [PPN]X salts. Ruff and Schlientz [18] have proposed the procedure of its synthesis which follows the brutto-equation

$$3PPh_3 + 2Cl_2 + NH_2OH \cdot HCl \longrightarrow [(Ph_3P)_2N]Cl + OPPh_3 + 4HCl$$

Similarly, [PPN]Br has been obtained recently using Br_2 instead of Cl_2 [20].

According to the procedure of the synthesis of [PPN]Cl [18] a precise amount of Cl_2 (2 M) is passed through the PPh_3 (3 M) solution in 1,1,2,2-tetrachloroethane at −20 to −30 °C. After completion of chlorination, $NH_2OH \cdot HCl$ (1 M) is introduced into the reaction, the mixture is boiled for 6–8 h and then [PPN]Cl is isolated in the solid phase. It is shown in ref. 18 that the yield of the final product depends on the amount of triphenylphosphine charged. When the reaction was carried out with 3 M the yield was 92% and at 0.3 M it decreased to 65–85%.

Despite high yields and a well developed technique [18], the procedure of the [PPN]Cl synthesis shows disadvantages caused by: (i) high chlorine activity and necessity to perform the reaction at low temperature and (ii) difficulty of chlorine proportioning.

It has been shown earlier that PCl_5 can be used as a 'solid equivalent' for chlorine in reactions of oxidizing chlorination of different types of complexes (see refs. 24–33). It is also known that the PCl_5 reaction with PPh_3 at a 1:1 molar ratio of reagents results in a mixture of the products PCl_3, Ph_3PCl_2 and $[Ph_3PCl](PCl_6)$; a slight amount of PPh_3 remains unreacted [34]. It has been established that PCl_5 can effectively replace Cl_2 in the [PPN]Cl synthesis. The reaction is described by the following equation

$$3PPh_3 + 2PCl_5 + NH_2OH \cdot HCl \longrightarrow [(Ph_3P)_2N]Cl + OPPh_3 + 2PCl_3 + 4HCl$$

Product A isolated as a result of the synthesis (see 'Experimental') contains a [PPN]Cl mixture (85% based on data analysis for Cl) and also $[PPN]^+$ salts with P-containing anions. The mixture is easily soluble in water and addition of HCl, HNO_3 or HBr to its aqueous solution leads to isolation in the solid phase of [PPN]Cl, $[PPN](NO_3)$ and [PPN]Br, respectively. The yield of pure [PPN]Cl was 72% for a charge of 0.3 M PPh_3 which is comparable with that of [PPN]Cl in the synthesis with Cl_2.

The synthesis with PCl_5 as the chlorinating reagent has its advantages because the oxidation stage of PPh_3 proceeds without special cooling and PCl_5 itself is a commercially available solid which can be easily dosed.

In conclusion it should be noted that the [PPN]Cl synthesis can result from the reaction of $OPPh_3$ deoxygenation through PCl_5 in 1,1,2,2-tetrachloroethane, subsequent removal of the $OPCl_3$ formed and addition of PPh_3 and $NH_2OH \cdot HCl$ to the mixture. The yield of [PPN]Cl in such a synthesis is no more than 10% and this reaction apparently is of no preparative importance. However, it is of interest that in the synthesis of [PPN]Cl the same reagent (PCl_5) can be either a chlorinating or deoxygenating substance depending on the choice of the other reagents.

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