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An economical small-scale synthesis of the μ-nitridobis(triphenylphosphonium) cation, [PPN]$^+$

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Abstract

Substitution of bromine for chlorine in the literature procedure for the preparation of the μ-nitridobis(triphenylphosphonium) cation allows the scale to be considerably reduced without serious loss of yield, and effects a significant reduction in the overall cost of the synthesis.

Discussion

Following its initial discovery by Appel and Hauss [1] and the development of a high-yield practical synthesis by Ruff and Schlientz [2] the μ-nitridobis(triphenylphosphonium) cation, $[Ph_3P{=}N{=}PPh_3]^+$ (commonly abbreviated to [PPN$^+$ [3]) has proved to be an extremely useful addition to the chemist's arsenal. The [PPN]$^+$ cation has found applications in the isolation and stabilisation of transition metal carbonyl anions [2] and forms stable non-hygroscopic salts with a variety of main group inorganic [3,4] and organic or organometallic anions [3,5]. The cation has also proven to be especially useful as a counter-anion which provides highly crystalline salts of large anions for structural studies. Recent examples include $[Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)]^-$ (X = Cl, Br, I, NO_2) [6] and the unusual [B–Cl–B]-bridged 1,8-naphthalenediylbis(dichloroborane)chloride anion [7], some earlier structural studies have been summarised [8]. [PPN]$^+$ salts have also been found to exhibit catalytic effects on the substitution reactions of ruthenium cluster complexes [9] and to be useful reagents for the introduction of reactive inorganic anions such as $[CN]^-$ [10] and $[NO_2]^-$ [11] into organic reaction media. Moreover physicochemical studies [12] have shown that [PPN]$^+$ salts in general show interesting behaviour in solution.

$$2Ph_3P + 2Cl_2 \rightarrow 2Ph_3PCl_2 \qquad (1)$$

$$2Ph_3PCl_2 + Ph_3P + [H_3NOH]Cl \rightarrow [(Ph_3P)_2N]Cl + Ph_3PO + 4HCl \qquad (2)$$

The Ruff and Schlientz synthesis of [PPN]$^+$ is a two-stage process (eq. 1 and 2).

In the first step Cl_2 from a lecture-bottle is introduced into a solution of Ph_3P in 1,1,2,2-$C_2H_2Cl_4$. The amount added is carefully monitored by measuring the loss of weight in the lecture bottle [2]. On the 3-molar scale described by Ruff and Schlientz excellent yields are obtained (ca. 92%). However, reducing the scale to 0.3 molar can cause the yield to drop to as low as 65% because of increased difficulty in accurately measuring the weight of chlorine [2]. We have found that this problem is eliminated by simply replacing chlorine by bromine in the synthetic procedure. Accurate monitoring of liquid bromine by volume or weight presents no problems in small-scale syntheses. Furthermore since the stainless steel cylinder and valve required for chlorine are now unnecessary the cost per mole of halogen used is reduced by ca. 75–85% thus effecting a major saving in the overall cost of the synthesis. A further advantage of this procedure is that the use of a low-temperature ($-30°$) bath is not required. Although the simultaneous presence of both chloride and bromide ions in the reaction mixture of the modified synthesis might be expected to lead to a mixture of [PPN]Cl and [PPN]Br, the chloride appears to be preferentially volatilised as HCl (cf. eq. 2) and the product is essentially pure [PPN]Br. We have routinely prepred [PPN]Br in 85% purified yield on a ca. 0.1 molar scale by this method.

Experimental

μ-Nitridobis(triphenylphosphonium) bromide

Triphenylphosphine (30.3 g, 0.115 mol) and 1,1,2,2-tetrachloroethane (40 ml) are placed in a 150 ml 3-neck flask fitted with magnetic stirrer, pressure-equalised addition funnel and nitrogen inlet. A liquid-paraffin bubbler is attached to the condenser and the system is flushed with nitrogen and cooled in an ice-bath. Bromine (12.3 g, 0.077 mol) is added to the cooled stirred solution during ca. 30 min. The ice-bath is replaced by a heating mantle and hydroxylamine hydrochloride (2.68 g, 0.04 mol) is added. The solution is brought to the boil and refluxed gently until hydrogen halide evolution has ceased (ca. 8 h). Work-up as described by Ruff and Schlientz [2] gives crude [PPN]Br as a pale yellow powder. In a typical preparation, after one recrystallisation from hot water the white product weighed 20.2 g (85%) and had m.p. 253–254 °C (lit. [3] 253-255 °C).

Found: C, 69.93; H, 4.74; Br 12.79; N, 2.21, $C_{36}H_{30}BrNP_2$ calcd.: C, 69.91; H, 4.89; Br, 12.92; N, 2.26%.

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