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CHEMISTRY

Synthesis of Tris(2-pyridyl)phosphine from Red Phosphorus and 2-Bromopyridine in the CsF–NaOH–DMSO Superbasic System

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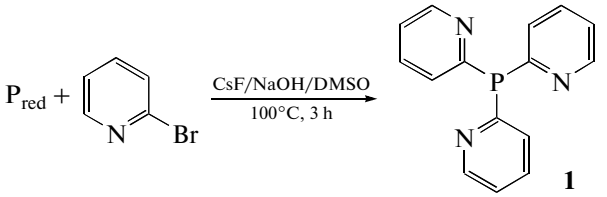
Pyridylphosphines are widely used as polydentate chemolabile P,N ligands for the design of multipurpose metal-complex catalysts [1–3], highly reactive building blocks in organic synthesis [4], and precursors in the preparation of new pharmaceuticals [5, 6]. Among pyridylphosphines, tris(2-pyridyl)phosphine is of special interest as a tripodal ligand of chelating type due to the geminal arrangement of the nitrogen atoms with respect to the phosphorus atom. Metal complexes obtained from tris(2-pyridyl)phosphine are efficient catalysts for industrially important processes, such as alkene hydroformylation [7], ethylene polymerization [8], methoxycarbonylation of acetylenes [9], and diene synthesis [10].

The known methods of preparation of tris(2-pyridyl)phosphine based on the reactions of pyridyllithium [11] or pyridylmagnesium halides [12] with phosphorus chlorides are multistep and require special experimental conditions (low temperatures, high-purity anhydrous solvents, isolation of the target phosphine by column chromatography [11] or by solid–liquid extraction with a large amount of diethylamine [12]).

In this report, we disclose a fundamentally new convenient method for the synthesis of tris(2-pyridyl)phosphine **1** by the direct reaction of red phosphorus with 2-bromopyridine in the presence of a strong base produced in the CsF–NaOH–DMSO system, which was previously used successfully in the reactions of nucleophilic addition to triple bond [13, 14]. The reaction occurs on heating the reagents (100°C, 3 h) in an inert atmosphere to give phosphine **1** in 57% yield (not optimized).



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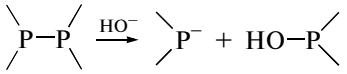
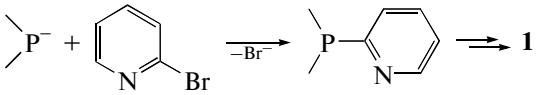
The reaction seems to proceed via initial cleavage of the red phosphorus macromolecule under the action of hydroxide anions to form phosphide anions that further react with 2-bromopyridine according to the nucleophilic substitution scheme.





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The revealed reaction opens a convenient approach to the one-pot synthesis of tris(2-pyridyl)phosphine, a ligand necessary for the design of metal complexes and a starting reagent to construct supramolecular structures and pharmaceuticals. Obtained data provide a fundamental contribution to the development of new methodology of synthesis of organophosphorus compounds by the direct phosphorylation of electrophiles with elemental phosphorus in the presence of strong bases [15].

EXPERIMENTAL

The IR spectrum was recorded as KBr pellets on a Bruker IFS-25 spectrophotometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained with a Bruker DPX-400 spectrometer (operating at 400.13, 101.61, and 161.98 MHz, respectively) using hexamethyldisiloxane as an internal reference and 85% H_3PO_4 as an external reference (^{31}P NMR). All experimental

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manipulations were carried out in an inert atmosphere (argon).

A suspension of 3.1 g (100 mmol) of red phosphorus, 4.0 g (100 mmol) of NaOH, 15.2 g (100 mmol) of CsF, 40 mL of DMSO, and 7.9 g (50 mmol) of 2-bromopyridine was heated to 100°C and stirred for 3 h at this temperature, and then cooled; 60 mL of water was added, and the mixture was extracted with chloroform (3 × 40 mL). The organic extract was washed with water (3 × 15 mL) and dried with potassium carbonate, the solvent was distilled off, and the residue was exposed to vacuum to give 2.52 g (yield 57%) of phosphine **1** as a colorless crystalline powder, mp 115–116°C (isopropanol) (lit. [11]: mp 113°C).

IR (KBr, ν, cm^{-1}): 3039, 2961, 2900, 1572, 1558, 1450, 1424, 1413, 1283, 1276, 1147, 1085, 1045, 987, 960, 907, 896, 774, 765, 743, 721, 712, 618, 548, 513, 503, 496, 426, 407, 395.

^{1}H NMR ($CDCl_3$); δ, ppm, *J*, Hz): 7.18–7.23 (m, 3H, HC-5), 7.41 (d, 3H, HC-3, $^3J_{HH}$ 7.0 Hz), 7.58–7.64 (m, 3H, HC-4), 8.72 (d, 3H, HC-6, $^3J_{HH}$ 3.70 Hz).

^{13}C NMR ($CDCl_3$, δ_C, ppm): 122.5 (C-5), 128.9 (d, C-2, $^2J_{PC}$ 19.3 Hz), 135.6 (d, C-4, $^3J_{PC}$ 2.6 Hz), 150.1 (d, C-6, $^2J_{PC}$ 19.3 Hz), 161.5 (d, C-2, $^1J_{PC}$ 2.6 Hz).

^{31}P NMR ($CDCl_3$, δ_P, ppm): –1.86.

For $C_{15}H_{12}N_3P$ anal. calcd. (%): C, 67.92; H, 4.56; N, 15.84; P, 11.68. Found (%): C, 67.75; H, 4.38; N, 15.67; P, 11.43.

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REFERENCES

1. Barton, B.E. and Rauchfuss, T.B., *J. Am. Chem. Soc.*, 2010, vol. 132, pp. 14 877–14 885.
2. Liu, J., Jacob, C., Sheridan, K.J., et al., *J. Chem. Soc., Dalton Trans.,* 2010, vol. 39, pp. 7921–7935.
3. West, N.M., Labinger, J.A., and Bercaw, J.E., *Organometallics,* 2011, vol. 30, pp. 2690–2700.
4. Slagt, V.F., Kame, P.C.J., van Leeuwen, P.W.N.M., et al., *J. Am. Chem. Soc.*, 2004, vol. 126, pp. 1526–1536.
5. Luque-Ortega, J., Reuther, P., Rivas, L., et al., *J. Med. Chem.,* 2010, vol. 53, pp. 1788–1798.
6. Kharat, A.N., Bakhoda, A., Foroutannejad, S., et al., *Z. Anorg. Allg. Chem.*, 2011, vol. 637, pp. 1–6.
7. Kurtev, K., Ribola, D., Jones, R.A., et al., *J. Chem. Soc., Dalton Trans.*, 1980, pp. 55–58.
8. Karam, A., Tenia, R., Martinez, M., et al., *J. Mol. Catal. A: Chem.*, 2007, vol. 265, pp. 127–132.
9. Drent, E., Arnoldy, P., and Budzelaar, P.H.M., *J. Organomet. Chem.*, 1994, vol. 475, p. 247.
10. Kuo, C.-Y., Fuh, Y.-S., Shiue, J.-Y., et al., *J. Organomet. Chem.*, 1999, vol. 588, pp. 260–267.
11. Bowen, R.J., Garner, A.C., Berners-Price, S.J., et al., *J. Organomet. Chem.*, 1998, vol. 554, pp. 181–184.
12. Kluwer, A.M., Ahmad, I., and Reek, J.N.H., *Tetrahedron Lett.*, 2007, vol. 48, pp. 2999–3001.
13. Trofimov, B.A., Malysheva, S.F., Gusarova, N.K., et al., *Zh. Org. Khim.*, 2003, vol. 39, pp. 1428–1429.
14. Trofimov, B.A. and Gusarova, N.K., *Usp. Khim.,* 2007, vol. 76, pp. 550–570.
15. Trofimov, B.A. and Gusarova, N.K., *Mendeleev Commun.,* 2009, vol. 19, pp. 295–302.