

Tris(2-pyridyl)phosphine: a straightforward microwave-assisted synthesis from 2-bromopyridine and red phosphorus and coordination with cobalt(II) dichloride

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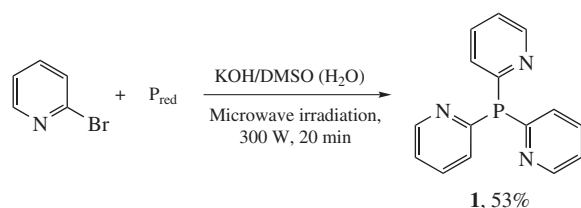
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Microwave irradiation of 2-bromopyridine with red phosphorus in the superbasic KOH/DMSO (H₂O) suspension affords tris(2-pyridyl)phosphine in 53% yield; two molecules of tris(2-pyridyl)phosphine coordinate with CoCl₂ by their six nitrogen atoms only to form [Co(2-Py₃P)₂]Cl₂·8H₂O complex having two phosphorus atoms beyond the coordination sphere.

Pyridylphosphines, in particular, tris(2-pyridyl)phosphine, attract a growing attention owing to the adjacent phosphorus and nitrogen atoms capable of a cooperative chelating with metal cations.¹ Now increasing applications of tris(2-pyridyl)phosphine in organic² and coordination^{1,3} chemistry are observed. Diverse ligations of tris(2-pyridyl)phosphine afford numerous novel and useful complexes,⁴ some of which catalyse hydroformylation of alkenes,⁵ ethylene polymerization,⁶ methoxycarbonylation of alkynes,⁷ and Diels–Alder synthesis.⁸

Currently, tris(pyridyl)phosphines are synthesized from pyridyl-lithium⁹ or pyridylmagnesium¹⁰ derivatives and phosphorus trichloride, with the target phosphine isolation requiring multistep tedious chromatography procedures⁹ or laborious solid–liquid extraction with large quantities of diethylamine.¹⁰

This communication deals with a straightforward one-pot preparation of tris(2-pyridyl)phosphine **1** which comprises the microwave-assisted reaction between commercially available 2-bromopyridine and red phosphorus in the superbasic KOH/DMSO (H₂O) suspension. The transformation was carried out under microwave irradiation (300 W) for 20 min at the molar ratio 2-bromopyridine:red phosphorus:KOH being 1:2:3, to afford the phosphine **1** in 53% yield (Scheme 1).[†]



[†] The ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker AV-400 spectrometer (400.13, 101.61 and 161.98 MHz, respectively) and referenced to H₃PO₄ (³¹P NMR) as external standard. FT-IR spectra were run on a Bruker Vertex 70 instrument. Microwave irradiation was performed in a microwave oven Samsung M181DNR (max power level 850 W) equipped with reflux condenser. All steps of the experiment were carried out in argon atmosphere. Red phosphorus, 2-bromopyridine, KOH (~15% water content) and DMSO (1% water content) were used as purchased.

The microwave assistance allows the reaction time to be substantially decreased as compared to the thermal version (100 °C, other conditions being the same) of the reaction (20 min vs. 3 h) though the yield has been somewhat lower (53 and 63%, respectively).

Apparently, the P_n macromolecule undergoes cleavage by the superbasic (less solvated) hydroxide ion to furnish the phosphorus centred anionic clusters **A** and neutral species **B**,¹¹ the former possessing a higher nucleophilicity due to the vicinity of several phosphorus atoms (α-effect). The supernucleophilic clusters of **A** type attack 2-bromopyridine to form C_{sp²}–P bond. The sequence of these nucleophilic substitution elemental steps continues until the formation of phosphine **1** (Scheme 2).

Phosphine **1** displays a rare coordination behaviour toward cobalt(II) dichloride in aqueous ethanol solution.[‡] In the complex formed, [Co(2-Py₃P)₂]Cl₂·8H₂O **2**, the cobalt centre coordinates with six nitrogen atoms of two molecules of tris(2-pyridyl)phosphine to give bis-phosphine cage structure with two phosphorus atoms oriented out of the coordination sphere (Figure 1).[§] The cobalt atom in complex **2** has a slightly distorted octahedral geometry with the octahedral faces being defined by the nature

Tris(2-pyridyl)phosphine 1. A mixture of 2-bromopyridine (7.90 g, 50 mmol), red phosphorus (3.10 g, 100 mmol), powdered KOH·0.5H₂O (10.00 g, 154 mmol), DMSO (50 ml) and H₂O (2 ml) was irradiated in microwave oven (300 W, temperature reached ~190–200 °C) for 20 min. The reaction mixture was cooled to room temperature, diluted with H₂O (60 ml) and extracted with CHCl₃ (3×20 ml). The chloroform extract was washed with H₂O (3×15 ml) and dried over K₂CO₃. The solvent was removed under reduced pressure and the residue was washed with cooled PrⁱOH (1×8 ml) and dried *in vacuo* (1 Torr) to give phosphine **1** as colourless microcrystalline powder. Yield, 2.34 g (53%), mp 115–116 °C (PrⁱOH) (lit.⁹ 113 °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. ¹H NMR (CDCl₃) δ: 7.18–7.23 (m, 3H, H-5), 7.41 (d, 3H, H-3, ³J_{HH} 7.0 Hz), 7.58–7.64 (m, 3H, H-4), 8.72 (d, H-6, ³J_{HH} 3.70 Hz). ¹³C NMR (CDCl₃) δ: 122.5 (C-5), 128.9 (d, C-2, ¹J_{PC} 19.3 Hz), 135.6 (d, C-4, ³J_{PC} 2.6 Hz), 150.1 (d, C-3, ²J_{PC} 19.3 Hz), 161.5 (C-6). ³¹P NMR (CDCl₃) δ: –0.06. Found (%): C, 67.82; H, 4.49; N, 15.71; P, 11.57. Calc. for C₁₅H₁₂N₃P (%): C, 67.92; H, 4.56; N, 15.84; P, 11.68.

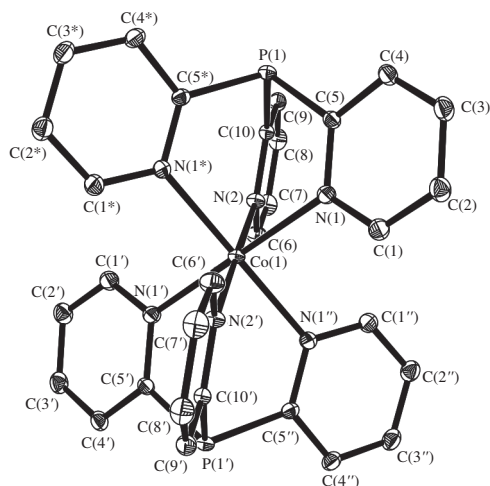
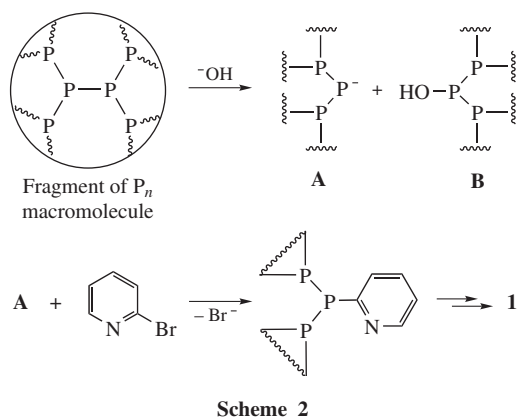


Figure 1 X-ray structure for the cation $[\text{Co}(2\text{-Py}_3\text{P})_2]^{2+}$ in complex **2**. Selected bond lengths (Å): Co(1)–P(1) 3.4840(5), Co(1)–N(1) 2.1614(9), Co(1)–N(2) 2.145(1), P(1)–C(10) 1.839(1), P(1)–C(5) 1.840(1).

of the bridgehead atom in phosphine **1**. The phosphorus atoms of the latter adopt a trigonal pyramidal geometry with the C–P bond lengths in the range of 1.839(2)–1.840(1) Å. It is worthwhile to mention that the Co(1)–N(2) distance in **2** [2.1449(12) Å] is

‡ *Bis[tris(2-pyridyl)phosphine]cobalt(II) dichloride octahydrate 2*. A mixture of tris(2-pyridyl)phosphine **1** (530 mg, 2.0 mmol) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (238 mg, 1.0 mmol) in 95% EtOH (15 ml) was stirred at 45–50 °C for 30 min to yield a red suspension. The latter was cooled to room temperature and the solid was filtered off. The resulting orange solution was allowed to stand overnight at 5–8 °C. The complex precipitated was filtered off, washed with EtOH–Et₂O (1:2) and dried *in vacuo* (1 Torr) to give orange crystals. Yield, 0.63 g (78%), mp 137–139 °C (decomp.). IR (film, ν/cm^{-1}): 3437, 3105, 3083, 3023, 2924, 2856, 1637, 1602, 1495, 1453, 1393, 1263, 1210, 1179, 1127, 1067, 1029, 1005, 944, 908, 855, 746, 697, 573, 512, 483. ^{31}P NMR (DMSO-*d*₆) δ : –1.72. Found (%): C, 44.67; H, 5.11; N, 10.39; P, 7.59. Calc. for $\text{C}_{30}\text{H}_{40}\text{Cl}_2\text{CoN}_6\text{O}_8\text{P}_2$ (%): C, 44.79; H, 5.01; N, 10.45; P, 7.70.

§ *Crystal data for 2*. Crystals of **2** ($\text{C}_{30}\text{H}_{40}\text{CoN}_6\text{P}_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{Cl}$, $M = 804.45$) are monoclinic, space group C_2/m , $a = 12.187(1)$, $b = 13.449(1)$ and $c = 11.455(1)$ Å, $\beta = 101.505(1)^\circ$, $V = 1839.8(3)$ Å³, $Z = 2$, $d_{\text{calc}} = 1.45$ g cm^{–3}, $\mu(\text{MoK}\alpha) = 0.754$ mm^{–1}, $2\theta_{\text{max}} = 55.04^\circ$. X-ray diffraction analysis was performed on a Bruker SMART APEX-II CCD diffractometer at 173 K [$\lambda(\text{MoK}\alpha) = 0.71073$ Å, ω -scans]. 6358 reflections were measured, from which 2112 reflections were independent, $R_1 = 0.023$ for 1990 reflections with $[F_0 > 4\sigma(F_0)]$. The structure was solved by direct methods and refined by a full matrix least-squares anisotropic procedure using SHELXTL97 programs.¹³

CCDC 863027 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2012.

approximately 0.02 Å shorter than the Co(1)–N(1) distance [2.1614(9) Å]. The Co(1)–P(1) distance is 3.4840(5) Å. Note that complex **2** is a rare example of cobalt ‘sandwich’ pyridylphosphine complexes. Hitherto, only few representatives of these complexes were prepared.¹²

In conclusion, a novel straightforward one-pot microwave-assisted preparation of tris(2-pyridyl)phosphine in a yield of up to 53% from available 2-bromopyridine and red phosphorus in the superbasic KOH/DMSO (H₂O) suspension has been disclosed. Thus, tris(2-pyridyl)phosphine is now gaining a position of an available phosphine ligand. Special ligation properties of this phosphine have been confirmed by the synthesis of complex $[\text{Co}(2\text{-Py}_3\text{P})_2]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ in which the two phosphorus atoms do not participate in coordination with the metal, while six pyridine nitrogen atoms are involved in the formation of a rare cage complex structure.

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Online Supplementary Materials

Supplementary data (details of ^1H , ^{13}C and ^{31}P NMR spectra of phosphine **1** and crystallographic data for complex **2**) associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.06.004.

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