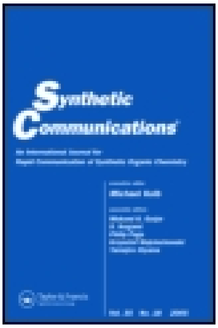

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A Simple Procedure for the Preparation of 1,8-BIS(Diphenylphosphino)Naphthalen

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SYNTHETIC COMMUNICATIONS, 25(11), 1741-1744 (1995)

A SIMPLE PROCEDURE FOR THE PREPARATION OF 1,8-*BIS*(DIPHENYLPHOSPHINO)NAPHTHALENE

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Abstract:
1,8-*Bis*(diphenylphosphino)naphthalene has been obtained in good yields from 1,8-dilithionaphthalene and chlorodiphenylphosphine.

1,8-*Bis*(diphenylphosphino)naphthalene has potential significance as a bidentate C_3-ligand in transition metal catalysed reactions. Recently, Jackson *et al.*[1] published the preparation of the bis-phosphine for its potential use in the palladium(II) catalysed ethene-CO-copolymerisation. We recently discovered that this ligand has a high catalytic activity in both the cyanation of vinylic halides (activity comparable to 1,1'-*bis*(diphenylphosphino)ferrocene, DPPF) and in the alkylation of heteroaromates (activity comparable to 1,2-*bis*(diphenylphosphino)ethane, DPPE)[2].

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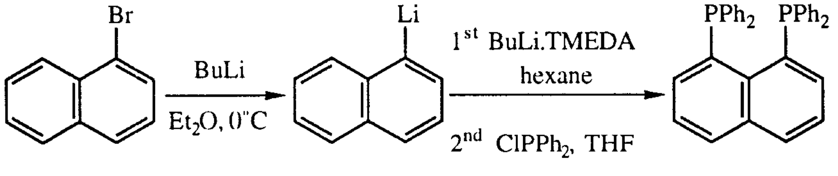
The synthesis of 1,8-*bis*(diphenylphosphino)naphtalene described by Jackson *et al.* started with 1,8 dibromonaphtalene, a compound whose synthesis is laborious[3]. We here report a more simple procedure for the preparation of the title compound, based upon the following scheme[4]:



Experimental procedure

All operations, including the work up are carried out under inert gas, as the product is air-sensitive. All solvents are deoxygenated by repeated evacuation and successive admission of nitrogen.

A 1-l round-bottomed, three-necked flask, fitted with a gas inlet, a mechanical stirrer and a gas outlet is perfused with nitrogen. Dry diethyl ether (80 ml, dried over machine-powdered potassium hydroxide and subsequently filtered) and a solution of 0.12 mol of *n*-butyllithium in ~75 ml of hexane are placed in the flask. The mixture is cooled down to -20°C, after which 0.10 mol (20.7 g) of bromonaphthalene is added in one portion. The cooling bath is removed and the temperature allowed to rise to +10°C. Stirring at this temperature is continued for an additional 15 min. The white suspension is cooled to -10°C and stirring is stopped. After settling of the solid material, as much as possible of the supernatant clear solution is decanted, while passing nitrogen through the flask (removal of the solution by means of a syringe is also possible). Dry hexane (200 ml, cooled at -10°C) is then added with manual swirling and the suspension is allowed to settle again. After cautiously decanting the clear solution, this operation is repeated three times. Subsequently a solution of 0.13 mol of *n*-butyllithium in ~82 ml of hexane is added to the remaining concentrated suspension, followed by 0.14 mol (16.0 g) of *N,N,N',N'*-tetramethylethane diamine (dried by distilling it from lithium alanate in a vacuum of ~100 torr). The stirrer is replaced with a reflux condenser and the third neck closed with a stopper. The upper end of the condenser is connected with a washing bottle filled with paraffin oil. The mixture (initially turbid solution) is heated under reflux until the evolution of gas (butane) has stopped completely (3 to 4 h) and the paraffin oil threatens to be sucked back (the slow stream of nitrogen passed through the flask is temporarily stopped in order to notice this). The

Table 1. ^{13}C NMR data[a]

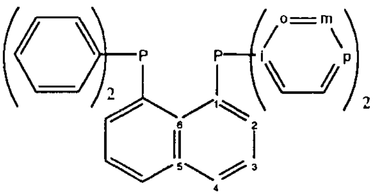
C	1	2	3	4	5	6	i	o	m	p
δ (ppm)	139.7	137.6	125.1	130.8	134.2	139.9	135.2	133.3	127.9	127.6
J_{CP} (Hz)	<2	<2			6.3	24.3	29.3	21.0	6.9	
pattern	s (broad)	s (broad)	s	s	t	t	(t)[b]	(t)[b]	(t)[b]	s

a. CD_2Cl_2 as solvent and internal standard δ 53.1 ppm

b. Virtual triplets because of J_{PP} > 100 Hz (Compare J_{PP} = 199 Hz in solid state[1])

yellowish-brown suspension of 1,8-dilithionaphthalene is cooled down to below 0°C and 100 ml of dry tetrahydrofuran (dried over machine-powdered KOH and subsequently distilled from $LiAlH_4$) is added with cooling below 0°C. The mixture is cooled to –80°C and a mixture of 0.25 mol (55.0 g, excess) freshly distilled chlorodiphenylphosphine and 50 ml of THF is added over 20 minutes, while keeping the temperature of the mixture between –50 and –70°C. After the addition the cooling bath is removed and the reaction mixture is allowed to rise to room temperature under stirring. A greyish-brown solution is formed. This is poured into 150 ml of water. After vigorous shaking, the layers are separated and a sufficient amount of dichloromethane is added to effect dissolution of the solid material. After drying the organic solution over $MgSO_4$ the solvent is removed under reduced pressure. The remaining solid is dissolved in 350 ml of benzene. The solution is warmed to ~60°C, after which dry methanol is added until crystals begin to separate. After warming to reflux in order to effect complete dissolution of the crystalline material, the solution is allowed to stand for 12 h at–5°C. The crystalline material is filtered off (in an inert atmosphere) on a sintered-glass funnel and rinsed twice with 50 -ml portions of dry methanol (0°C). After removal of the adhering solvent in a oil-pump vacuum there remain yellow crystals, yield 65 % (pure according to ^{13}C, ^{1}H and ^{31}P NMR). The mother liquid may afford an additional 5 % of crystals after concentration *in vacuo* and standing for several days at –5°C. M.p. 202 - 204°C (uncorrected, after crystallisation from benzene).

Numbering Scheme:



Spectral data (Bruker AC 300 spectrometer):
^{1}H-NMR (CDCl$_3$, internal standard δ 7.25 ppm): δ: 7.885 (H-4, broad dd, $^3J_{HH}$= 7.9 Hz, $^4J_{HH}$= 1.8 Hz, 2H); 7.422 (H-2, ddd, $^3J_{HH}$= 7.0 Hz, $^3J_{PH}$= 4.0 Hz., $^4J_{HH}$= 1.8 Hz, 2H); 7.381 (H-3, dd, $^3J_{HH}$= 7.9 Hz, $^3J_{HH}$= 7.0 Hz, 2H); 7.29-7.25 (H-o + H-p, multiplet, 12H); 7.18-7.24 (H-m, multiplet, 8H);
^{31}P-NMR (CDCl$_3$, PPh$_3$ at δ −6 ppm as external standard): δ: −15.3.
The X-ray data were in accordance with the structure (compare also ref. 1)

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