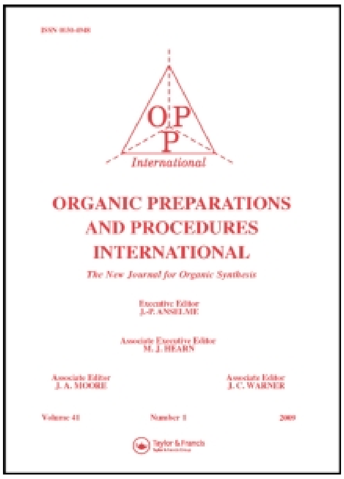

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cis-1,2-VINYLENEBIS (DIPHENYLPHOSPHINE)

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cis-1,2-VINYLENEBIS(DIPHENYLPHOSPHINE)

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$$ClP(Ph)_2 + 2Li \rightarrow (Ph)_2PP(Ph)_2 + 2LiCl$$

$$(Ph)_2PP(Ph)_2 + 2Li \rightarrow LiP(Ph)_2 + LiCl$$

$$2LiP(Ph)_2 + \underline{cis}\ CHCl = CHCl \rightarrow \underline{cis}(Ph)_2PCH = CHP(Ph)_2 + 2LiCl$$

cis-1,2-vinylenebis(diphenylphosphine) has been prepared by the formation of lithium diphenylphosphide from chlorodiphenylphosphine and subsequent reaction with cis-1,2-dichloroethene. This route is more advantageous than the lithium cleavage of triphenylphosphine for two reasons.[1] First, it is less time consuming and second, no phenyllithium is generated which consequently must be destroyed by t-butyl chloride. Incomplete removal results in lower yields of the diphosphine since both phenyllithium and lithium diphenylphosphide can react with cis-1,2-dichloroethene. The use of such a ditertiary phosphine in stabilizing the low valence oxidation states of transition metals has been amply noted in the literature.[2-5]

Experimental

To a clean, dry 250-ml three-neck flask containing 1.00 g (0.144 g-atoms) of finely chopped lithium suspended in 50 ml of tetrahydrofuran, is added slowly, with rapid stirring and under nitrogen, 9.5 ml (.05 mole) of chlorodiphenylphosphine in 20 ml of tetrahydrofuran over a period of about 1 hr.[6,7] Cleavage of the intermediate tetraphenylbiphosphine begins in approximately 5 min as evidenced by the red coloration of the pieces of lithium. After complete addition, an additional 20 ml of tetrahydrofuran is added and the solution is stirred for an extra 1.5 hrs before finally refluxing for 0.5 hr. The final solution at room temperature is deep red.

To a 150-ml dropping funnel of a second clean, dry 250-ml three-neck flask is added, under nitrogen, the red diphenylphosphide solution.[6] This solution is dropped slowly and carefully into the empty 250-ml flask in order to exclude any unreacted lithium from the final reaction mixture. Upon the slow addition of 1.9 ml (.025 mole) cis-1,2-dichloroethene in 10 ml of tetrahydrofuran to the rapidly stirred solution of diphenylphosphide at room temperature the red color is discharged greenish-red after 0.75 hr. Additional stirring under nitrogen for 0.75 hr at room temperature results in the final greyish brown solution.

The volume of the greyish-brown solution is reduced with a rotary evaporator under aspirator pressure and hot water bath temperature to about 20 ml. The resulting thick brown oil, upon addition to 500 ml of cold water containing a dissolved small pellet of NaOH,[8] yields a light brown solid which, upon separation from the mother liquor, may be recrystallized from large volumes of hot methanol, 95% ethanol, or absolute ethanol.[9] From 6-8 g (61 to 81%) of crude solid, slightly more than 3 g (30%) of pure cis-1,2-vinylenebis(diphenylphosphine) may be obtained as long white needles, mp 123-125°, lit.[1] 123-125°.

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6. A clean oxygen-free system is necessary to inhibit oxidation of the phosphine.
7. Aldrich chlorodiphenylphosphine was used without further purification. Tetrahydrofuran was dried over and distilled from calcium hydride. cis-1,2-dichloroethene was distilled and dried over magnesium sulfate.
8. Sodium hydroxide dissolves any diphenylphosphinic acid which forms.
9. These solutions should be stoppered since slow air-oxidation of the diphosphine has been noted in the past.

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