HETEROCYCLES, Vol. 30, No. 1, 1990

REACTION OF TRIHETEROARYLPHOSPHINES WITH ORGANOLITHIUM REAGENTS CONCURRENT LIGAND EXCHANGE AND LIGAND COUPLING

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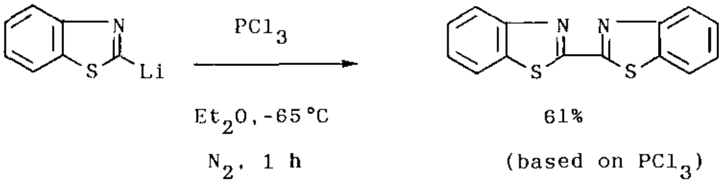
Abstract — Reaction of tri(2-benzothiazyl)phosphine or tri(2-pyridyl)phosphine with aryl- or heteroaryllithium compounds in THF affords 2,2'-bibenzothiazyl or 2,2'-bipyridyl by ligand coupling in good yields.

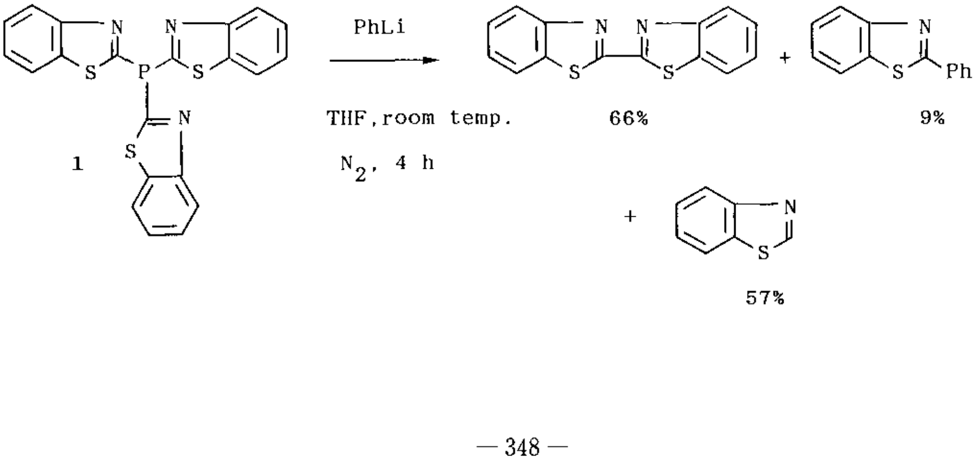
Earlier, we have suggested the concept of ligand coupling within hypervalent intermediate.[1] The hypervalent species are valence-expanded, hence known to undergo ligand exchange, ligand coupling and self-decomposition besides pseudo-rotation. We have also shown that there are concurrent and also consecutive ligand exchange and ligand coupling within hypervalent intermediates.[2-4] A typical example of concurrent ligand exchange and coupling would be the reaction between benzyldi(2-pyridyl)phosphine oxide with heteroaryllithium,[2] while a typical example of consecutive ligand exchange and coupling may be the reaction between alkyl 2-pyridyl sulfoxides and alkyl Grignard reagents.[3] As an extension of our works on the ligand coupling on phosphorus atom, we have examined the reactions of some triheteroarylphosphines with organolithium reagents and obtained interesting results. We now wish to report the coupling reaction, which takes place during the reaction of triheteroarylphosphines with organolithium reagents.[5]

The reaction of phosphorus trichloride with organometallic reagents has been widely used for the synthesis of tertiary phosphines. Although, tri(2-benzothiazyl)phosphine (1) can be prepared readily by treating 3 molar amounts of 2-trimethylsilylbenzothiazole with one molar amount of phosphorus trichloride, the earlier effort by Moore and Whithesides to obtain 1 directly by treating 2-benzothiazyllithium with phosphorus trichloride was unsuccessful.[6] However, they did not mention anything concerning the product of the reaction. We have reexamined the reaction of the lithium compound with phosphorus trichloride and found the reaction to yield a coupling product, i.e., 2,2'-bibenzothiazyl as a major product (Equation 1).



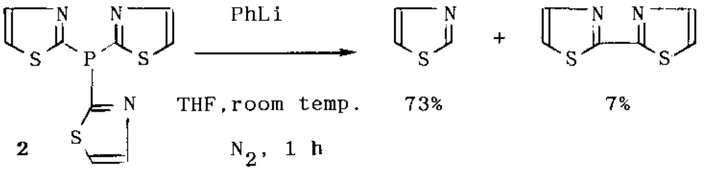
(1)

In order to examine, if the triheteroarylphosphine which resulted in the reaction of PCl_3 with the lithium reagent undergoes subsequent reaction with the lithium reagent to afford the coupling product, the reaction of 1 with lithium reagents was carried out. When 1 was treated with an equimolar amount of phenyllithium in THF at room temperature for 2 h under nitrogen atmosphere, 2,2'-bibenzothiazyl and 2-phenylbenzothiazol, ligand coupling products, were formed in 62% and 9% yields, respectively, together with ligand exchange product, benzothiazol (Equation 2). 2,2'-Bibenzothiazyl was also found to yield in the reaction of the phosphine with an equimolar amount of 2-pyridyllithium or 2-benzothiazyllithium in 62% and 40% yields, respectively. Therefore, the reaction of 2-benzothiazyllithium with phosphorus trichloride is considered to involve concurrent ligand exchange as well as prior ligand exchange and

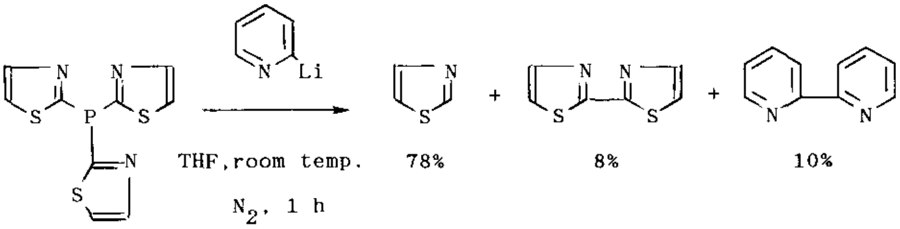


(2)

subsequent ligand coupling. Similarly, di(2-benzothiazyl)phenylphosphine reacted with an equimolar amount of phenyllithium to afford 2,2'-bibenzothiazyl, 2-phenylbenzothiazol, and benzothiazol in 52, 24, and 58% yields, respectively. Tri(2-thiazyl)phosphine (**2**) can be readily prepared by treating thiazyllithium with phosphorus trichloride.[6] In the case of tri(2-thiazyl)phosphine, however, treatment with an equimolar amount of phenyllithium at room temperature gave mainly ligand exchange product, and a minor amount of ligand coupling product, 2,2'-bithiazyl (Equation 3). Use of 2-pyridyllithium gave not only the major *ligand exchange product, thiazol, but also two kinds of the* ligand coupling products, 2,2'-bithiazyl and 2,2'-bipyridyl, under the same conditions (Equation 4).

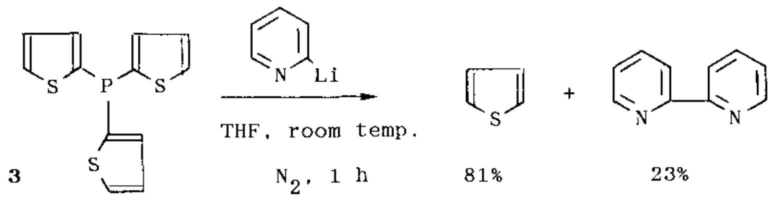


(3)



(4)

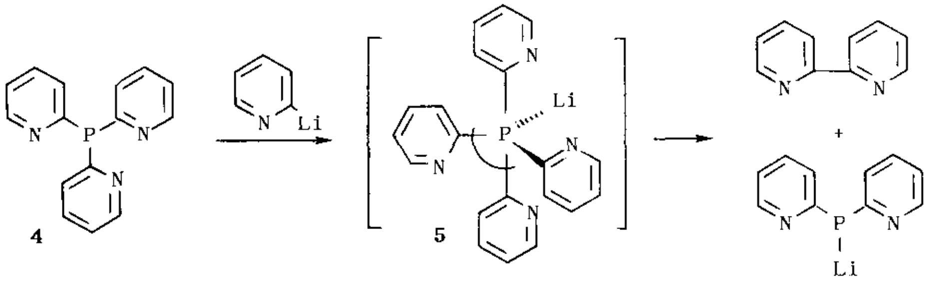
Tri(2-thienyl)phosphine (**3**) can also readily be made by the reaction of 2-thienyllithium with phosphorus trichloride.[6] 2-Thienyl group has been considered to be the best leaving group in the alkaline hydrolysis of heteroarylphosphonium salts,[7] or in the reaction of tri(2-thienyl)phosphine oxide with organolithium reagent.[2] Indeed, **3** was found to react with phenyllithium affording only the ligand exchange product in a good yield. In this reaction, no coupling product was observed. Meanwhile, the reaction with 2-pyridyllithium gave both the ligand exchange product and the ligand coupling product, i.e., thiophene and 2,2'-bipyridyl (Equation 5).



(5)

In the Equations 4 and 5, the formation of 2,2'-bipyridyl can be interpreted by consecutive ligand exchange and ligand coupling. This would be supported by the following reaction in which two 2-pyridyl groups tend to couple giving 2,2'-bipyridyl in a good yield.

We have also examined the reaction of tri(2-pyridyl)phosphine (**4**) with 2-pyridyllithium.[8] When **4** was treated with an equimolar amount of 2-pyridyllithium in THF at room temperature for 3 h, 2,2'-bipyridyl was formed in 81% yield. The reaction with two equivalents of the lithium reagent at room temperature for 18 h gave 2,2'-bipyridyl in nearly a quantitative yield.



Scheme 1

The results mentioned above would show that the ligand exchange and the ligand coupling reaction proceeds via an pentacoordinated phosphorus intermediate. A plausible mechanism for the reaction of **4** with 2-pyridyllithium is shown in Scheme 1. Nucleophilic attacking of the lithium reagent on the phosphorus atom would give the intermediate (5). Within the intermediate, the equatorial 2-pyridyl group would couple with the axial 2-pyridyl group to yield 2,2'-bipyridyl.

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5) The reaction of tertialy phosphines with organolithium reagents was reported by Kyba, in which ligand exchange raction took place. E. P. Kyba, J. Am. Chem. Soc., 1975, 97, 2554; E. P. Kyba, J. Am. Chem. Soc., 1976, 98, 4806.

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8) A typical procedure for the reaction of the phosphines with organolithium reagents is as follows: To a solution of tri(2-pyridyl)phosphine (2 mmol) in dry THF (40 ml) was added an ethereal solution of 2-pyridyllithium (2 mmol) under N_2 atmosphere. The reaction mixture was stirred for 3 h at room temperature and then quenched with water (1 ml). After the addition of biphenyl (100 mg) as an internal standard, the mixture was subjected to glc analysis.

Received, 30th August, 1989