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# Biphenylic Bisphosphines through *ortho*-Metalation of Aryldiphenylphosphine Oxides

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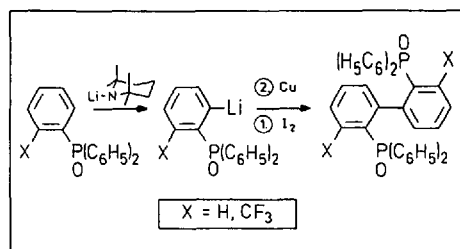
**Abstract.** Diphenyl-(2-trifluoromethyl)phosphine oxide was metalated next to the diphenylphosphinoyl group with LITMP. Upon iodination and *Ullmann* coupling, the corresponding 3,3'-disubstituted bis(phosphine oxide) was obtained. When phenyllithium was used as metalating agent, aryl/phenyl group exchange occurred. The torsional barrier for the planarization of the biaryl moiety was equal to  $22 \pm 1$  kcal/mol.

The *ortho*-lithiation of triphenylphosphine oxides [1] has opened a new entry to atropisomeric biphenylic bisphosphines [2]. This reaction was also the key step for the unequivocal synthesis of 2,2'-(diphenylphosphino)biphenyl [3], the simplest member of this family.

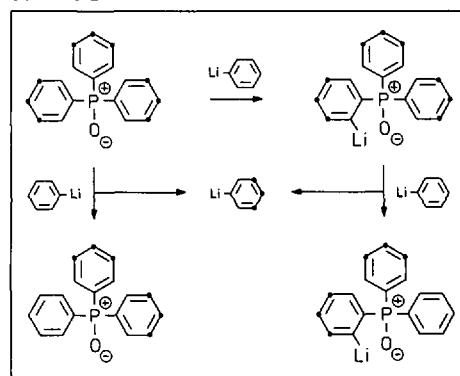
In the hope of identifying new possibilities for ligands preparations, we have undertaken some studies. The first curiosity was to find out whether aryldiphenylphosphine oxides could be selectively metalated on the ring carrying an electron withdrawing group such as trifluoromethyl and, if so, at which position. Indeed selective metalation proved to be possible in the case of diphenyl(2-trifluoromethylphenyl)phosphine oxide. Lithiation adjacent to the diphenylphosphinoyl group was performed with lithium tetramethylpiperidide (LITMP) followed by iodination and *Ullmann* coupling to afford the corresponding 3,3'-disubstituted bis(phosphine oxide).

The bis(trifluoromethyl) substituted bis(phosphine oxide) could be resolved with *O,O'*-dibenzoyltartaric acid. However, with an activation energy of  $22 \pm 1$  kcal/mol for the planarization of the biaryl moiety, rapid racemization occurred already at room temperature when one of the antipodes was solubilized in dichlorome-

Scheme 1



Scheme 2



thane. The unsubstituted 2,2'-(diphenylphosphino)biphenyl and its bis(phosphine oxide) were reported [4] to have identical racemization barriers of 22 kcal/mol. This coincidence points to a cogwheel motion coupling the untwisting of the central biaryl core and the 6,6'-hydrogens with rotations around the P-*ortho* bonds. Therefore, the buttressing effect due to the 3,3'-bis(trifluoromethyl) substitution has no significant consequence on the activation energy for the planarization.

If phenyllithium was used as metalating agent [1] instead of the LITMP, the (trifluoromethyl)phenyl group was re-

placed by phenyl to give triphenylphosphine oxide and 2-(trifluoromethyl)phenyllithium. So far only alkyl/phenyl exchange was known [5]. In order to demonstrate that even a phenyl could be replaced by an other phenyl group, we used a triphenylphosphine oxide carrying deuterium labels at all *meta*- and *para*-positions [4] and let it react with non-deuterated phenyllithium [6]. The metalated phosphine oxide was carboxylated to obtain the corresponding acid. The deuterium content of the latter was followed as a function of time. Unexpectedly, instead of a normal asymptotic curve from the initial value 9 to the average value of 6 deuteriums, a jump occurred when 40–50% of the 2-(diphenylphosphinoyl)phenyllithium was formed. A possible explanation of this anomaly could be the higher propensity of the *o*-lithiated triphenylphosphine oxide to undergo phenyl/phenyl exchange compared with the triphenylphosphine oxide itself. An addition-elimination mechanism through a pentavalent intermediate was postulated for the alkyl/phenyl exchange [5][7]. Considering the addition of phenyllithium on the *o*-lithiated triphenylphosphine oxide, the intermediate should be stabilized by chelation between the *o*-lithium and the O-atom. This stabilization should lead to an acceleration of the phenyl/phenyl exchange process as compared with the non-lithiated triphenylphosphine oxide.

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